Main-Chain-Type 8-Quinolinol Polymers: Synthesis, Optical Properties, and Complex Formation with Metals

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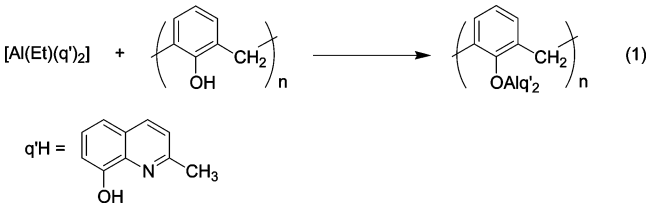
ABSTRACT: Poly(aryleneethynylene)-type polymers containing 8-quinolinol (qH) units in their main chain were prepared via Pd-catalyzed polycondensation. They were first obtained as $-SiMe_2{}^tBu$ group protected polymers, and the $-SiMe_2{}^tBu$ protected polymer had number average molecular weights (M_n) of 4000−13000. Deprotection of the $-SiMe_2{}^tBu$ group with $[NBu_4]F$ gave the 8-quinolinol polymers. The polymers exhibited photoluminescence with a peak at about 470 nm and quantum yields of 15−49%, and the photoluminescence was tuned by addition of metal ions such as Zn^{2+} and Al^{3+}. Reaction of the polymer with $[Al(Et)(q')_2]$ (q′ = 2-methyl-8-quinolinolato) gave an Alq_3-type polymer complex, which was also photoluminescent in solutions and film.

Introduction

8-Quinolinol and its derivatives provide a variety of luminescent complexes.[1] Very recently, the use of aluminum and zinc complexes of 8-quinolinol (e.g., Alq_3 (q = 8-quinolinolato)) in organic light emitting diodes (OLEDs) has attracted much interest,[2] and OLEDs using Alq_3-type complexes have been industrialized. Alq_3 is an electron transporting and luminescent material,[2] and modifications of the 8-quinolinolato ligand to improve the OLED performance of the Al complex have actively been carried out.[3] For example, an Al complex with 2-methyl-8-quinolinolato ligand serves as an excellent hole blocking material.[4]

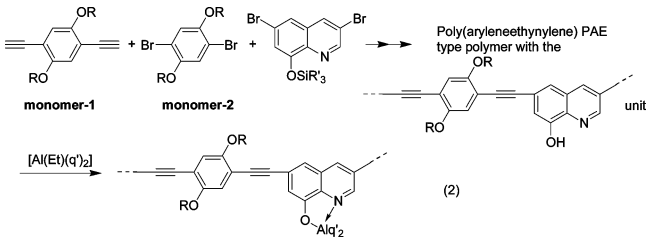
Recently, we reported that an Al complex $[Al(Et)(q')_2]$ (q′ = 2-methyl-8-quinolinolato) with a reactive Al−Et bond could be isolated by choosing the appropriate ligand q′ and that $[Al(Et)(q')_2]$ reacted with active OH compounds such as 8-quinolinol and H_2O to give various luminescent aluminum complexes.[5]

In the reaction with a phenolic resin, $[Al(Et)(q')_2]$ gives luminescent $Al(q')_2$-containing polymer materials.[5a]



Alq_3-type complexes are usually used in OLEDs via a vapor deposition process. However, obtaining polymeric materials containing the Alq_3-type complex may enable convenient, low-cost, and scaleable manufacturing methods (e.g., spin-coating and ink-jet printing methods). Blending polymers with Alq_3[6] and connecting Alq_3 in polymer side chains[7] have been carried out. Recently, fabrication of OLEDs was also carried out using cross-linked Alq_3-containing polymers prepared by photopolymerization of a vinyl monomer having the Alq_3-type complex.[8]

Synthesis of polymers containing the Alq_3-type complex in the main chain, however, has received less attention.[9,10] We now report the preparation of poly(aryleneethynylene) (PAE)-type polymers containing the 8-quinolinol units via Pd-catalyzed polycondensation, their optical properties, and the reaction of the polymers with metal compounds, e.g.,



Polymers having a large π-conjugation system in the main chain are the subject of recent interest.[11] A part of the results was reported in the communication form.[9]

Experimental Section

Materials. 1,4-Didodecyloxy-2,5-diethynylbenzene (monomer-1), 1,4-dibromo-2,5-didodecyloxybenzene (monomer-2), 5,7-dibromo-8-(*t*-butyldimethylsiloxy)quinoline (monomer-a), 3,6-dibromo-8-(*t*-butyldimethylsiloxy)quinoline (monomer-b), 3,7- dibromo-8-(*t*-butyldimethylsiloxy)quinoline (monomer-c), and $Pd(PPh_3)_4$ were prepared as previously reported.[9] 1,4-Bis(2-ethylhexyloxy)-2,5-diethynylbenzene (monomer-3),[12] 1,4-dibromo-2,5-bis(2-ethylhexyloxy)benzene (monomer-4),[13a] 2,7-diethynyl-9,9-dioctylfluorene (monomer-5),[13] 2,7-dibromo-9,9-dioctylfluorene (monomer-6),[14] and 5,7-dibromo-8-methoxyquinoline[15] were prepared according to the literature.

Measurements. NMR and IR spectra were recorded on a JEOL EX-400 spectrometer and a JASCO-IR 460 spectrophotometer, respectively. UV−vis and photoluminescence (PL) spectra were measured using a 3100PC spectrometer and a Hitachi F-4010 spectrometer, respectively. Gel permeation chromatography (GPC) was carried out with a Shimadzu LC-9A liquid chromatograph using chloroform as the eluent. X-ray diffraction (XRD) patterns of the polymers were obtained by using a RINT 2100 Ultima+/PC X-ray diffractometer. The XRD patterns were measured at a reflection

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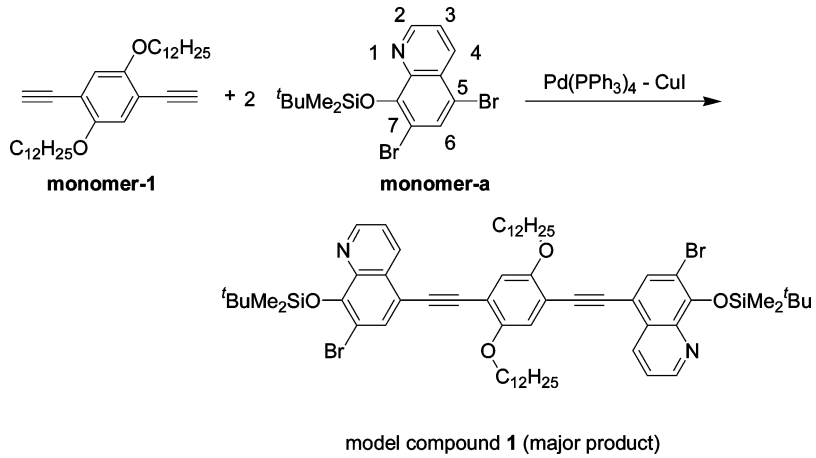
Scheme 1. 1:2 Reaction Between Monomer-1 and Monomer-a



mode. Elemental analyses were carried out with a Yanagimoto Type MT-2 CHN autocorder.

Reaction with Metal Ions, Acid, and Base. Methanol solutions of the metal compounds were added to a $CHCl_3$/methanol solution of the polymer. The final mixed solution for UV−vis and PL measurements was adjusted to a 4:1 (v/v) $CHCl_3$/methanol solution. For example, a methanol solution (1 mL) of $ZnCl_2$ (1.0×10^{-3} M, 1.0×10^{-3} mmol) was added to a 4:1 (v/v) mixed solution (10 mL) of $CHCl_3$ and methanol containing polymer-4a(6/4-OEH) (0.1 mg, 1.0×10^{-4} mmol of the 8-quinolinol unit). To the above solution, 100 mL of $CHCl_3$ and 24 mL of methanol were added to obtain a 4:1 (v/v) $CHCl_3$/methanol solution containing $ZnCl_2$ and polymer-4a(6/4-OEH). $AlCl_3$, $ZnCl_2$, $MgCl_2$, $PdCl_2$, NaOH, and CF_3COOH were used as the reactant.

Synthesis of Model Compound 1. To a 25 mL Schlenk-type flask, charged with 1,4-didodecyloxy-2,5-diethynylbenzene (monomer-1, 124 mg, 0.25 mmol), 5,7-dibromo-8-(*t*-butyldimethylsiloxy)-quinoline (monomer-a, 209 mg, 0.50 mmol), $Pd(PPh_3)_4$ (29 mg, 0.025 mmol), and CuI (5 mg, 0.025 mmol), was added triethylamine (5 mL) and toluene (10 mL) under nitrogen. The mixture was stirred for 0.5 h at room temperature and at 70 °C for 12 h. After removal of the solvent by evaporation, the residue was washed with an aqueous solution of NaCl and the product was extracted with $CHCl_3$. The $CHCl_3$ solution was condensed by evaporation, and a mixture of oligomers and the model compound **1** was obtained by column chromatography on a SiO_2 column (eluent = $CHCl_3$). The product was purified by HPLC (eluent = $CHCl_3$) to afford **1** as a yellow solid, yield = 20 mg (7%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ): 8.83 (dd, $J_{24} = 2.0$ Hz, $J_{23} = 4.0$ Hz, 2H, 2-H-Q), 8.81 (dd, $J_{42} = 2.0$ Hz, $J_{43} = 8.0$ Hz, 2H, 4-H-Q), 7.95 (s, 2H, 6-H-Q), 7.47 (dd, $J_{32} = 4.0$ Hz, $J_{34} = 8.0$ Hz, 2H, 3-H-Q), 7.08 (s, 2H), 4.11 (t, 4H, $J = 6.8$ Hz), 1.96 (m, 4H), 1.57−1.20 (m, 36 H), 1.13 (s, 18H, *tert*-Bu), 0.87 (t, 6H, $J = 6.8$ Hz), 0.39 (s, 12H, -Si−CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, δ): 153.52, 151.27, 148.07, 140.70, 135.02, 134.58, 128.97, 121.67, 115.62, 113.62, 113.47, 111.74, 91.25, 90.97, 69.36, 31.97, 29.72, 29.71, 29.68, 29.60, 29.41, 26.22, 26.18, 22.76, 19.60, 14.21, and −2.42. The molecular structure of the model compound **1** was confirmed by X-ray crystallography as described below. ^{13}C{^{1}H} NMR spectrum of the model compound **1** is shown in the Supporting Information.

Synthesis of Polymers. Synthesis of the precursor polymers with the $-SiMe_2{}^tBu$ (^{t}Bu = *tert*-butyl) protecting groups (cf. Scheme 2) and a polymer containing 8-methoxyquinoline units was carried out according to the $Pd(PPh_3)_4$-catalyzed polycondensation in a 1:3 (v/v) mixture of NEt_3 and toluene (cf. Scheme 2) using mixtures of the diethynyl monomer (monomer-1, monomer-3, or monomer-5), the comonomer (monomer-2, monomer-4, or monomer-6), and the dibromo monomer (monomer-a, monomer-b, monomer-c, or 5,7-dibromo-8-methoxyquinoline). The ratios between the monomers are shown in Schemes 2 and 3, and 10 mol % of the Pd-$(PPh_3)_4$ catalyst and 10 mol % of CuI cocatalyst were added based on per diethynyl monomer. The polymerization was carried out by stirring the reaction mixture for 60 h at 70 °C. The reaction mixture was poured into methanol, and the obtained polymer was separated by filtration and dried under vacuum. Deprotection of the $-SiMe_2{}^t$-Bu group was carried out by treating the protected polymer with $[NBu_4]F$.[9,16] ^{1}H NMR data of the protected polymers, 8-methoxyquinoline polymer, and deprotected polymers are shown in the Supporting Information.

Synthesis of Alq′$_2$−Polymer Complex. To a THF solution of polymer-4(OEH) was added dropwise a THF solution of [Al(Et)-(q′)$_2$]. The reaction mixture was stirred at room temperature for 1 h and at 50 °C for 17 h. After being cooled to room temperature, the solution was poured into methanol. The precipitate was separated by filtration, washed with methanol and acetone, and dried under vacuum to obtain the Alq′$_2$−polymer complexe polymer-6(OEH-Al).

X-ray Crystallographic Analysis of the Model Compound 1. A crystal suitable for X-ray diffraction study was obtained by recrystallization of the compound from a $CHCl_3$/hexane solution and was mounted on a glass capillary tube on a Rigaku AFC-7R automated CCDC diffractometer equipped with Mo Kα radiation ($\lambda = 0.7107$ Å). The data were collected to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected. A sweep of data was done using ω scans from −110.0° to 70.0° in 0.5° steps at $\chi = 45.0°$ and $\phi = 0.0°$. The detector swing angle was −20.38°. A second sweep was performed using ω scans from −110.0° to 70.0° in 0.5 ° steps at $\chi = 45.0°$ and $\phi = 90.0°$. The crystal−detector distance was 285 mm. Readout was performed in the 0.070 mm pixel mode. Calculations were carried out by using the program package teXan for Windows. The structure was solved by heavy-atom Patterson methods (DIRDIF92 PATTY) and expanded using Fourier techniques. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. Crystal data ($C_{64}H_{90}Br_2N_2O_4Si_2$): $M = 1167.39$; triclinic; $P1$ (No. 2); $a = 16.775(9)$, $b = 17.18(1)$, and $c = 18.69(1)$ Å; $\alpha = 87.74(3)$, $\beta = 73.41(2)$, and $\gamma = 77.78(2)°$; $V = 5040(5)$ Å^3; $Z = 3$; $\mu = 12.93$ cm^{-1}; $F(000) = 2004$; $D_{calcd} = 1.239$ g m^{-3}; number of unique reflections = 20 859; number of used reflections ($I > 2\sigma(I)$) = 6565; number of variables = 1020. The final R and R_w values were 0.094 and 0.071, respectively. $R = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2)/\Sigma w F_o^2]^{1/2}$.

Results and Discussion

Synthesis of a Model Compound 1. The following Pd-catalyzed 1:2 condensation reaction between monomer-1 and monomer-a gave the model compound **1** as shown in Scheme 1 (cf. Experimental Section).

The ^{1}H NMR spectrum of the reaction mixture indicated that the reaction gave **1** in about 50% yield.

The molecular structure of **1** was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy and X-ray crystallography. Figures 1

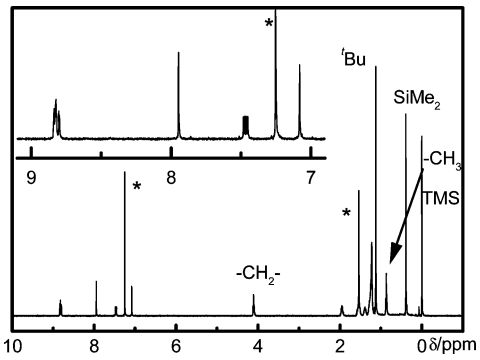


Figure 1. ^{1}H NMR spectrum of the model compound **1** in $CDCl_3$. The peaks with * are due to solvent impurities ($CHCl_3$ and H_2O). For assignment of the peaks in the aromatic region, see the Experimental Section.

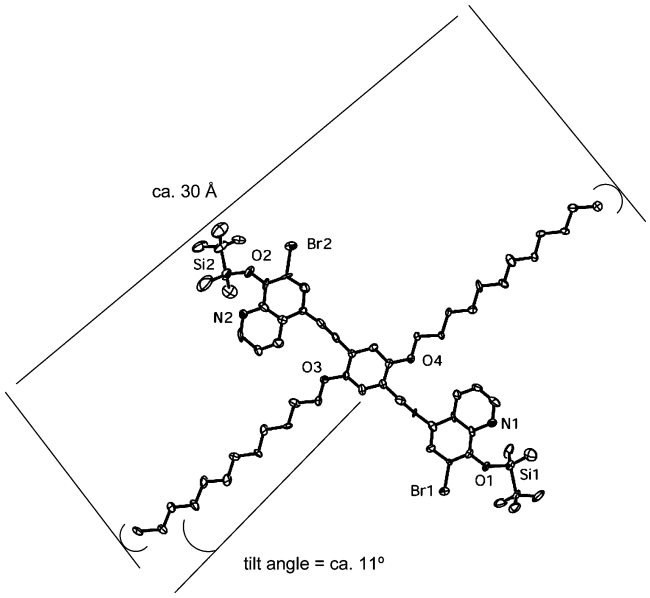


Figure 2. Molecular structure of the model compound **1**. The terminal−terminal distance of the two $-OC_{12}H_{25}$ groups is about 30 Å including the van der Waals radius of the terminal CH_3 group. The π-conjugation system essentially has a coplanar structure. The $-OC_{12}H_{25}$ side chain is tilted by about 11° from the main chain. According to the tilt, the effective terminal−terminal distance of the $-OC_{12}H_{25}$ group becomes 30 Å × cos 10° (ca. 29 Å).

and 2 exhibit the ^{1}H NMR spectrum and the molecular structure of the model compound, respectively. The data shown in Figures 1 and 2 give basis for the assignment of ^{1}H NMR peaks of $-SiMe_2{}^t$Bu protected polymers described below and for understanding the molecular structure of the polymers obtained in this study. $^{13}C\{^1H\}$ NMR spectrum of **1** is shown in the Supporting Information.

The fact that **1** is obtained as the major product suggests higher reactivity of the C−Br bond at the 5-position than the C−Br bond at the 7-position toward the organometallic condensation. The presence of the neighboring bulky $-OSiMe_2{}^t$Bu group seems to retard the reaction of the C−Br bond at the 7-position toward the Pd-complex used as the catalyst.

Polymerization. The following Pd-catalyzed polycondensations[11] shown in Scheme 2 were carried out between diethynyl monomers and dibromo monomers. To avoid possible coupling reaction between the 8-quinolinol −OH group and the −C≡CH or the −C−Br group, the −OH group was protected by the $-SiMe_2{}^t$Bu group.

The polymers were obtained in 63−97% yields. In the polymerization shown in Scheme 2, the dibromo comonomer (monomer-2 or monomer-4) was added in addition to the $-SiMe_2{}^t$Bu protected 8-quinolinol monomer (monomer-a through monomer-c). The ratio between the comonomer and the $-SiMe_2{}^t$Bu protected 8-quinolinol monomer was either 6:4 or 8:2. Without the comonomer, the obtained PAE-type homo polymers were insoluble despite the presence of the bulky $-SiMe_2{}^t$Bu group in the polymer, and characterization of the homopolymer was difficult.

The polymers obtained from monomer-a and monomer-b had good solubility in organic solvents such as THF and $CHCl_3$. However, polymer-1c(6/4-OC12) obtained from monomer-c was only partly soluble in organic solvents (e.g., about 50% in $CHCl_3$), and GPC data of polymer-1c(6/4-OC12) were obtained with the $CHCl_3$-soluble part. The polymer derived from monomer-c is considered to have a straight molecular structure, and its stiff structure seems to make the polymer less soluble.

As another type of polymer, the following PAE-type polymer composed of 8-methoxyquinoline unit was also prepared, and its chemical properties were investigated (Scheme 3). Table 1 summarizes synthetic results of the polymers 1, 2, and 3. The obtained polymers showed M_n values of of 4000−13 000 in the GPC analysis.

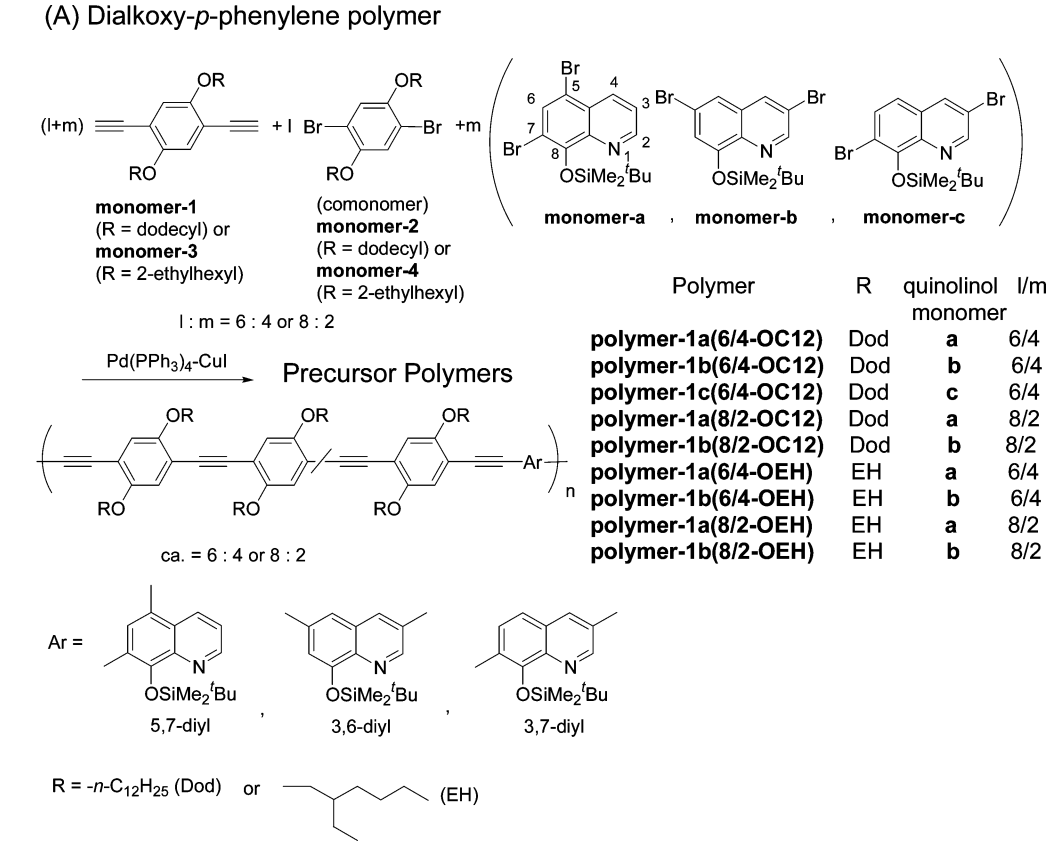
The M_n value of 13 000 for polymer-1a(6/4-OEH) corresponds to the incorporation of 20 monomeric units from monomer-3, 12 monomeric units from monomer-4, and 8 monomeric units from monomer-a into the polymer chain; there data indicate that polymer-1a(6/4-OEH) contains about 40 aromatic units. Analogously, polymer-1a(8/2-OEH) with a molecular weight of 12 600 is formed from about 20 monomer-3, 16 monomer-4, and 4 monomer-a units. The soluble part of polymer-1c(6/4-OC12) contains less number of the monomeric units, and the insoluble part is considered to have a higher molecular weight than the soluble part.

IR and ^{1}H NMR spectra of the polymers are reasonable for the molecular structure of the polymers, and ^{1}H NMR data are given in the Supporting Information. The IR spectra show a $\nu_{C\equiv C}$ peak at about 2200 cm^{-1}. The acetylenic ν_{C-H} peak of the diethynyl monomer at about 3290 cm^{-1} and the ν_{C-Br} peak of the dibromo monomer at about 1100 cm^{-1} are not observable in the IR spectra. The ^{1}H NMR data indicate that the molecular structure of the polymers essentially agrees with the feed ratio (l:m in Scheme 2) of the two dibromo monomers.

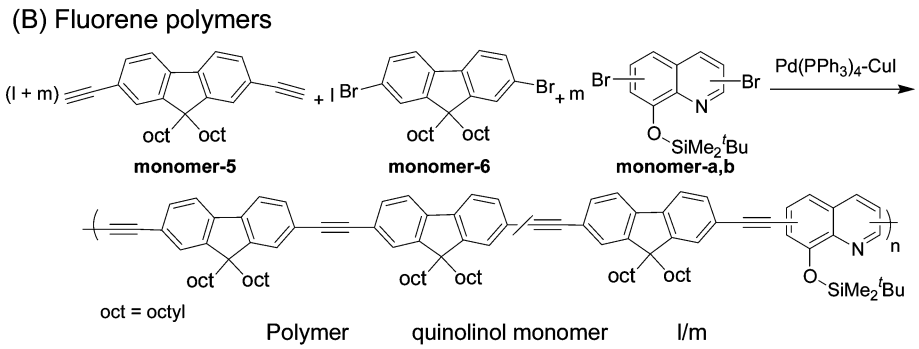
Formation of an Ordered Structure of the Polymers Containing the $-OC_{12}H_{25}$ Group. Figure 3a exhibits a powder XRD pattern of the polymer-1a(6/4-OC12). The XRD pattern shows a peak in a low angle region at d = 28.7 Å. Such a peak in the low angle region is often observed with linear π-conjugated polymers having long alkyl or alkoxy side chains and has been assigned to a distance between the π-conjugated main chains separated by the long side chains.[11a−c] The main chain of the polymer-1a(6/4-OC12) is considered to bend at the 8-quinolinol unit; however, the polymer is considered to have some linear parts, and the linear parts seem to form an end-to-end (not interdigitation) packing[11a−c] which is depicted in the top part of Figure 3.

The distance of 28.7 Å agrees well with the effective terminal-to-terminal distance (29 Å) of the two $-OC_{12}H_{25}$ side groups which is described in the caption of Figure 2. The repeating height h (estimated to be about 6.8 Å from the CPK model, cf. the top part of Figure 3) of the main chain and the effective diameter of the alkoxy side chain (ϕ = ca. 4.2 Å) make the formation of an interdigitation packing mode[11a−c] difficult. The broad background diffraction at d = 4.25 Å is consid-

Scheme 2. Synthesis of −SiMe$_2$^{t}Bu Protected Precursor Poly(aryleneethynylene) PAE-Type Polymers

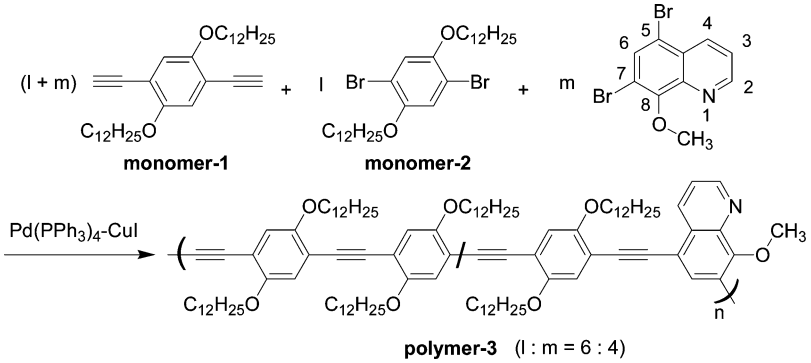


Polymer	R	quinolinol monomer	l/m
polymer-1a(6/4-OC12)	Dod	**a**	6/4
polymer-1b(6/4-OC12)	Dod	**b**	6/4
polymer-1c(6/4-OC12)	Dod	**c**	6/4
polymer-1a(8/2-OC12)	Dod	**a**	8/2
polymer-1b(8/2-OC12)	Dod	**b**	8/2
polymer-1a(6/4-OEH)	EH	**a**	6/4
polymer-1b(6/4-OEH)	EH	**b**	6/4
polymer-1a(8/2-OEH)	EH	**a**	8/2
polymer-1b(8/2-OEH)	EH	**b**	8/2



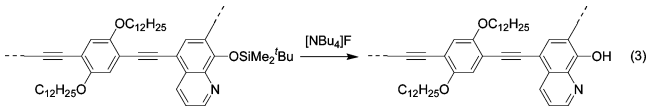
Polymer	quinolinol monomer	l/m
polymer-2a(6/4)	**a**	6/4
polymer-2b(6/4)	**b**	6/4
polymer-2a(8/2)	**a**	8/2
polymer-2b(8/2)	**b**	8/2

Scheme 3. Preparation of the 8-Methoxyquinoline Polymer, Polymer-3



ered to have various interferences related to 4.25 Å between various atoms (e.g., C, N, O, and Si) in the polymer solid. As shown in Figure 3b, the packing structure of the polymer in solid is essentially maintained after deprotection of the polymer-1a(6/4-OC12) to polymer-4a(6/4-OC12) with the 8-quinolinol unit.

The XRD pattern of polymer-1b(6/4-OC12) shows similar peaks at d = 29.4 and 4.26 Å.



(3)

In contrast to the case of $-OC_{12}H_{25}$ polymers, the −OEH (EH = 2-ethylhexyl) polymers (cf. Scheme 2) showed only a broad XRD peak in the low angle region at about 15 Å, as shown in Figure S1 in the Supporting Information. The branched −OEH alkoxy side chain seems to make formation of an ordered packed structure difficult.

Deprotection of the $-SiMe_2{}^tBu$ Group. The precursor $-OSiMe_2{}^tBu$ protected polymers were deprotected by treatment of the polymer with $[NBu_4]F$, as shown in Scheme 4. Deprotection of $-SiR_2R'$ groups of organic compounds with $[NBu_4]F$ has been reported.[16]

IR spectra of the deprotected polymers show a ν_{O-H} peak of the hydroxyl group of the 8-quinolinol unit at about 3420 cm^{-1} and a $\nu_{C\equiv C}$ peak at about 2200 cm^{-1}. The ^1H NMR peak of the $-SiMe_2{}^tBu$ group disappeared completely after the deprotection. The ^1H NMR spectra of polymer-4b(6/4-OEH) and polymer-4b(8/2-OEH) show a new peak at δ 8.05, which was assigned to the −OH proton of the 8-quinolinol unit. These results support the fact that deprotection reaction occurred smoothly.

Most of the polymers having alkoxy side chains, polymer-4a(6/4-OC12), polymer-4b(6/4-OC12), polymer-4a(8/2-OC12), polymer-4a(6/4-OEH), polymer-4b(6/4-OEH), and polymer-4a-(8/2-OEH), were soluble in organic solvents such as chloroform and THF. However, polymer-4c(6/4-OC12) with a straight structure, polymer-4b(8/2-OC12), polymer-4b(8/2-OEH), and polymers having the fluorene unit, polymer-5s (cf. Scheme 2 and Scheme 4), were only partly soluble in organic solvents. Because of good solubility and relatively higher molecular weights of polymer-4b(6/4-OC12) and polymer-4a(6/4-OEH), the metal-complexation study described below was mainly carried out with these polymers.

UV−vis and Photoluminescence (PL) Data. The longest UV−vis absorption peaks of the 8-quinolinol polymers were observed in a range from about 410 to 430 nm. The UV−vis absorption peak (λ_{max}) was shifted to a longer wavelength from those of the corresponding monomers (e.g., 339, 300, and 322 nm for monomer-1, monomer-2, and monomer-a, respectively) because of expansion of the π−conjugation system.

The λ_{max} values of the $-SiMe_2{}^tBu$ protected polymers essentially were in agreement with those of the deprotected 8-quinolinol polymers, revealing that the $-SiMe_2{}^tBu$ protecting group did not have a significant effect on the electronic state of the polymer. The straight polymer, polymer-1c(6/4-OC12), may be expected to show λ_{max} at a longer wavelength than those of the bent polymers, polymer-1a(6/4-OC12) and polymer-1b-(6/4-OC12). However, the former polymer shows λ_{max} (392 nm) at a shorter wavelength than those (λ_{max} = 417 and 403 nm, respectively) of the latter polymers. These results seem to be due to the lower molecular weight of the soluble part of polymer-1c(6/4-OC12) compared to those of polymer-1a(6/4-OC12) and polymer-1b(6/4-OC12) and suggest that the λ_{max} value saturates at a relatively short π-conjugation length, which is broken at the bent 8-quinolinol-5,7-diyl or 8-quinolinol-3,6-diyl unit. The 8-methoxyquinoline polymer, polymer-3, shows λ_{max} near to those of the $-SiMe_2{}^tBu$ protected polymers and the deprotected polymers. The polymers having the fluorene unit, polymer-2a(6/4), polymer-2b(6/4), polymer-2a(8/2), and polymer-2b(8/2), show λ_{max} at 382, 386, 384, and 389 nm, respectively.

Table 1. Preparation of the Polymers[a]

polymer	yield, %	M_n[b]	M_w/M_n[b]
polymer-1a(6/4-OC12)	79	6200	1.9
polymer-1b(6/4-OC12)	91	11000	1.8
polymer-1c(6/4-OC12)	63	4000[c]	2.8[c]
polymer-1a(8/2-OC12)	89	7700	2.5
polymer-1b(8/2-OC12)	91	11000	2.1
polymer-1a(6/4-OEH)	85	13000	3.1
polymer-1b(6/4-OEH)	77	10400	3.0
polymer-1a(8/2-OEH)	90	12600	1.9
polymer-1b(8/2-OEH)	97	8500	2.7
polymer-2a(6/4)	82	4000[c]	2.3[c]
polymer-2b(6/4)	83	9500[c]	3.2[c]
polymer-2a(8/2)	78	5100[c]	2.7[c]
polymer-2b(8/2)	74	10500[c]	4.4[c]
polymer-3	97	6000	1.3

[a] Carried out at 70 °C for 60 h in a mixture of NEt_3 and toluene (1:3, v/v) in the presence of 10 mol % of $Pd(PPh_3)_4$ and CuI per diethynyl monomer. [b] Estimated from GPC (eluent = chloroform, polystyrene standards, M_n = number average molecular weight, M_w = weight average molecular weight). [c] Data for the $CHCl_3$-soluble part (cf. the text).

All the polymers were photoluminescent, and the UV−vis and PL data of the polymers are shown in Table 2.

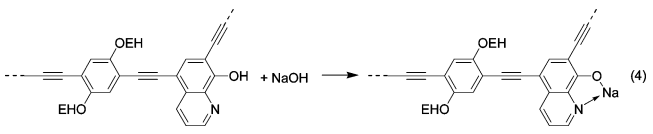
In the film, the λ_{max} values of polymer-3 and polymer-4(OC12)s are shifted by about 30 nm to the longer wavelength from the λ_{max} values observed in $CHCl_3$, suggesting the presence of an intermolecular electronic interaction between the polymer molecules with the $-OC_{12}H_{25}$ side chains in the solid state. However, such a shift is not obvious for the polymers containing the branched alkoxy side chains, polymer-4(OEH)s. These polymers containing the branched alkoxy side chains do not seem to have an effective intermolecular electronic interaction in the solid state because of effective separation of the polymer molecules due to the presence of the bulky OEH side chains.

The 8-quinolinol polymers gave quantum yields ranging from 15 to 49% in photoluminescence in chloroform. The PL peak shifts to a longer wavelength in the films, as shown in Table 2, suggesting that the polymers form an excimer-like adduct between the photoactivated polymer and the polymer in the ground state in the solid state.

Reaction with Metal Ions. It is known that 8-quinolinol forms complexes with metal ions. Metal complexes with a large π-conjugated ligand system have been the subject of recent intrest.[17,18]

Addition of metal ions to a 4:1 (v/v) $CHCl_3$−methanol solution of polymer-4a(6/4-OEH) caused a change in the PL spectrum. Figure 4 exhibits examples of the changes in the PL spectrum on addition of metal ions to a $CHCl_3$−methanol solution of the polymer-4a(6/4-OEH). The data on UV−vis and PL response are given in Table 3.

As shown in Figure 4, Na^+ and Al^{3+} lead to the formation of a new PL peak at about 550 nm, and the tone of the emitted light was somewhat varied (cf. the inset of Figure 4). Formation of salts of polymer-4a(6/4-OEH) with the metal ion is suggested, e.g.,



(4)

The PL of polymer-4a(6/4-OEH) was almost quenched by Pd^{2+}, as shown in Figure 4; a similar quenching effect was reported for a π-conjugated polymer of 1,10-phenanthroline.[18]

In contrast to the case of polymer-4a(6/4-OEH), the addition of metal ions to a 4:1 (v/v) $CHCl_3$−methanol solution of

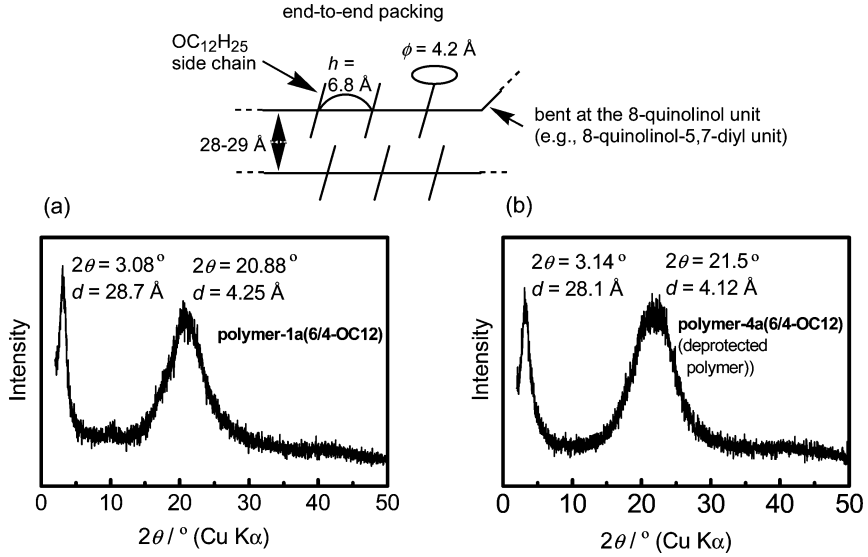


Figure 3. Powder XRD patterns of (a) polymer-1a(6/4-OC12) and (b) polymer-4a(6/4-OC12) obtained after deprotection of polymer-1a(6/4-OC12). A model for an end-to-end packing part is shown above the XRD patterns. The linear part of the polymer is considered to form the end-to-end packing, and the main chain is considered to be bent at the 8-quinolinol unit such as the 8-quinolinol-5,7-diyl unit. h = Repeating length of the unit formed from monomer-1 and monomer-2. ϕ = Diameter of the $-OC_{12}H_{25}$ side chain.

Scheme 4. Deprotection of the Precursor Polymers

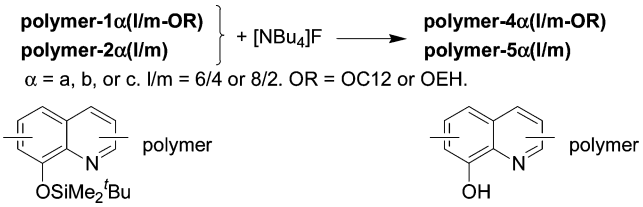


Table 2. Optical Data of the Polymers

	solution, peak wavelength in nm		ϕ in soln[b], %	thin film, peak wavelength in nm	
polymer	UV−vis	PL[a]		UV−vis	PL[a]
polymer-3	416	471 496(s)	24	439	511 529
polymer-4a(6/4-OC12)[c]	418	472	19	447	504(s) 548
polymer-4b(6/4-OC12)[c]	401	466	26	419	500
polymer-4a(8/2-OC12)	428	474 502(s)	15	454	565
polymer-4b(8/2-OC12)	417	472 501(s)	35	447	521 558
polymer-4a(6/4-OEH)	423	472	34	429	491 536
polymer-4b(6/4-OEH)	413	471	49	417	486 522
polymer-4a(8/2-OEH)	426	475	32	428	493(s) 550
polymer-4b(8/2-OEH)	427	476	34	437	490 526
polymer-6a(6/4-OEH−Al)	419	472	22	425	473 507
polymer-6b(6/4-OEH−Al)	413	471	54	445	474 504(s)
polymer-6a(8/2-OEH−Al)	435	474	25	439	570
polymer-6b(8/2-OEH−Al)	433	476	37	442	493 529

[a] Photoluminescence measured under N_2, (s) indicates a shoulder peak. When two values are given, the two peaks have comparable intensities. [b] Quantum yield of photoluminescence in chloroform calculated based on a quinine sulfate standard in 0.5 M sulfuric acid. [c] From ref 9.

polymer-4b(6/4-OEH), polymer-4a(8/2-OEH), and polymer-4b(8/2-OEH) caused smaller changes in the PL. The stronger response of polymer-4a(6/4-OEH) than that of polymer-4b(6/4-OEH) may have originated from the stronger acidity of the −OH group in polymer-4a(6/4-OEH) because of the presence of an electron-withdrawing ethynyl substituent at the *o*-position of the −OH group (cf. eq 4), and the lower response of polymer-4a(8/2-OEH) and polymer-4b(8/2-OEH) is considered to be due to a lower content of the 8-quinolinol unit. Figure S2 in the Supporting Information shows effects of NaOH on light emission of polymer-4a(6/4-OEH) and polymer-4b(6/4-OEH).

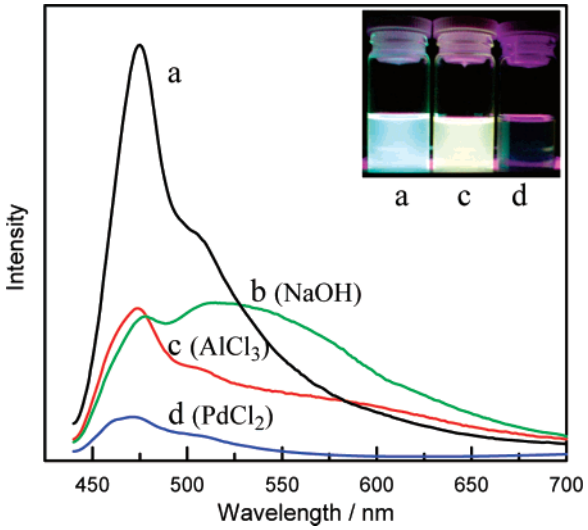


Figure 4. PL spectra and a photograph showing light emission of the polymer-4a(6/4-OEH) and its metal complexes in a 4:1 (v/v) mixed $CHCl_3$/methanol solution: (a) polymer-4a(6/4-OEH), (b) polymer-4a(6/4-OEH) in the presence of NaOH, (c) polymer-4a(6/4-OEH) in the presence of $AlCl_3$, and (d) polymer-4a(6/4-OEH) in the presence of $PdCl_2$. The PL spectra were obtained by excitation at the 421 nm. The photograph was taken under irradiation with light at 365 nm. N_2 was bubbled in the solution and the sample tube was sealed.

Addition of metal ions to a 4:1 (v/v) THF−methanol solution of polymer-4b(6/4-OC12) led to changes in the PL spectrum similar to those observed with polymer-4b(6/4-OEH). For example, addition of Al^{3+} brought about a shoulder emission peak at about 500 nm. The PL of polymer-4b(6/4-OC12) was also quenched by Pd^{2+}.

Table 3. UV−vis and PL Response of the Polymers to M^{n+} in a 4:1 (v/v) Mixed $CHCl_3$−Methanol Solution

	polymer-4a(6/4-OC12)			polymer-4a(6/4-OEH)			polymer-4b(6/4-OEH)		
metal ions	λ_{max} (nm)	λ_{EM} (nm)	Φ (%)	λ_{max} (nm)	λ_{EM} (nm)	Φ (%)	λ_{max} (nm)	λ_{EM} (nm)	Φ (%)
ion free	423	473	12	421	475	18	410	473	11
Al^{3+}	425	473[a]	7	422	473[a]	8	415	476[a]	19
Zn^{2+}	428	473[a]	6	426	473[a]	6	412	474[a]	10
NaOH	428	479, 539	16	430	478, 514	11	406	473	[b]
CF_3COOH	328	472	4	418	473	6	416	472	15
Pd^{2+}	431	quenched	[b]	423	471	3	417	472	4
Mg^{2+}	412	476, 526	9	428	474[a]	7	411	475[a]	5

[a] With the appearance of a shoulder peak at 520 nm. [b] Not determined.

Scheme 5. Polymer−Al Complex

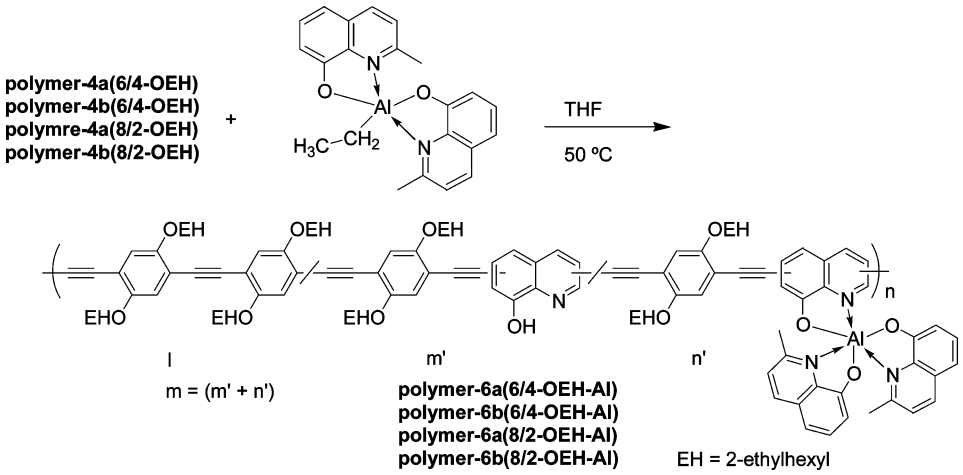
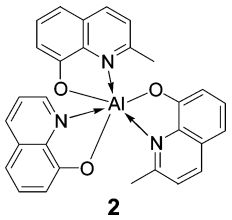


Chart 1. Structure of the $[Al(q')_2(q)]$ 2

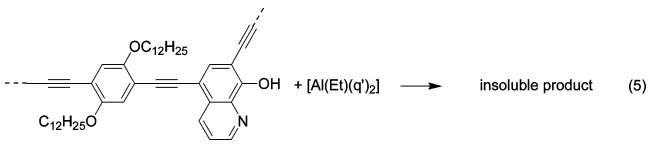


2

Polymer−Alq_3-Type Complexes. As described in Introduction, $[Al(Et)(q')_2]$ shown in eq 1 reacts with phenols and 8-quinolinol to give the corresponding aluminum complexes. For example, the Al complex reacts with 8-quinolinol to give an $[Al(q')_2(q)]$ complex (**2**) depicted in Chart 1;[5]

$$[Al(Et)(q')_2] + \text{8-quinolinol} \rightarrow \mathbf{2}.$$

Reaction of the 8-quinnolinol polymer with $[Al(Et)(q')_2]$ is expected to give a new photoluminescent polymeric aluminum complex. However, the polymeric aluminum complex obtained by the reaction of polymer-4a type having the $-OC_{12}H_{25}$ group (e.g, polymer-4a(6/4-OC12)) with $[Al(Et)(q')_2]$ was insoluble in organic solvents.



Kudo pointed out that the polymers having Alq_3-type pendant complexes often became insoluble due to cross-linking of the polymer.[7d] Because the Alq_3-type complex is a labile complex,

$$\underset{\text{labile}}{Alq_3} + \underset{\text{different 8-quinolinol}}{q''H} \rightarrow Alq_2(q'') + qH \quad (6)$$

a ligand exchange reaction is considered to cause the cross-linking, and this seems to make the obtained polymer−Alq_3-type complex insoluble.

To improve the solubility of the obtained polymer−Al complex, we carried out the reaction of polymer-4(OEH)s with $[Al(Et)(q')_2]$. The bulky OEH group in the main chain was expected to retard the intermolecular ligand exchange reaction. Scheme 5 shows the synthetic reaction of the polymer−Alq_3-type complex polymer-6(OEH-Al)s.

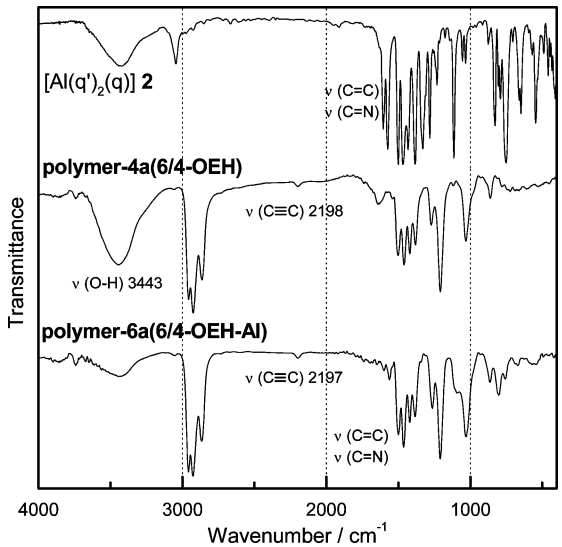


Figure 5. IR spectra of $[Al(q')_2(q)]$, polymer-4a(6/4-OEH), and the polymer−Alq_3-type complex polymer-6a(6/4-OEH−Al).

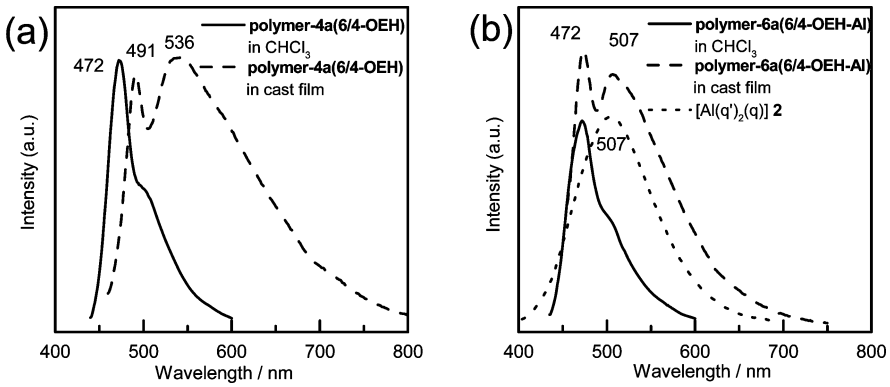


Figure 6. PL spectra of (a) polymer-4a(6/4-OEH) in $CHCl_3$ (solid line) and polymer-4a(6/4-OEH) in cast film (dashed line) and (b) polymer−Alq_3-type complex polymer-6a(6/4-OEH-Al) in $CHCl_3$ (solid line), polymer-6a(6/4-OEH-Al) in cast film (dashed line), and [Al(q′)$_2$(q)] **2** in $CHCl_3$ (dotted line) excited at the absorption wavelength (cf. Table 2).

Figure 5 shows the IR spectra of [Al(q′)$_2$(q)] **2**, polymer-4a-(6/4-OEH), and the polymer complex polymer-6a(6/4-OEH-Al).

In the IR spectrum of the polymer complex polymer-6a(6/4-OEH-Al), the ν(OH) peak at 3440 cm^{-1} becomes weaker than that of polymer-4a(6/4-OEH)**.** According to the reaction with [Al(Et)(q′)$_2$], the number of N in the polymer increased and the C/N atomic ratio of polymer-4a(6/4-OEH) decreased from 98.9 to 59.3 after the reaction with [Al(Et)(q′)$_2$]. The C/N atomic ratio of 59.3 corresponds to transformation of about 30% of the −OH group to −OAl(q′)$_2$ group as described in the Supporting Information.

Because the polymer-4a(6/4-OEH) derived from polymer-1a(6/4-OEH) is considered to contain eight 8-quinolinol units as described above, these results indicate that the polymer-6a-(6/4-OEH-Al) contains about two Al complexes in the polymer chain constituted of about 40 aromatic units (vide ante). In the reaction of [Al(Et)(q′)$_2$] with phenolic resins shown in eq 1, about one-half of the phenolic −OH groups were transformed to the −OAl(q′)$_2$ group.[5a] The XRD pattern of polymer-6a(6/4-OEH-Al) resembles that of polymer-4a(6/4-OEH) shown in Figure S1. However, the peak intensity of the peak at d = 15 Å becomes weaker for polymer-6(6/4-OEH-Al). The bulky Alq_3-type moiety in the polymer complex seems to make the formation of an ordered packed structure more difficult.

Although the solubility of the obtained polymer complexes, polymer-6(OEH-Al)s, was not high, the complexes were partly soluble in organic solvents (e.g., about 40% in boiling $CHCl_3$ and 30% in boiling *o*-dichlorobenzene). Hence, obtaining UV−vis and PL data in $CHCl_3$ and preparation of cast films of the polymer complexes polymer-6(OEH-Al)s were possible.

Emission from Alq_3-Type Center in Polymer−Al Complex. Figure 6 shows photoluminescence spectra of [Al(q′)$_2$-(q)] **2**, polymer-4a(6/4-OEH), and the polymer complex polymer-6a(6/4-OEH-Al).

As shown in Figure 6 and Table 2, both the polymer-4a(6/4-OEH) and its Al complex, polymer-6a(6/4-OEH−Al), give a main PL peak at 472 nm in $CHCl_3$. In the solution, the main emission seems to occur from the polymer chain part without the alumination. As described above, the polymer-6a(6/4-OEH-Al) is considered to contain two Al complexes in the polymer chain composed of many (about 40) aromatic units, and transfer of photoenergy captured by the aromatic polymer chain to the Al complex dose not seem to be fast in the single polymer molecule dissolved in $CHCl_3$. The photoenergy captured by the aromatic polymer chain is considered to be emitted from the aromatic polymer chain before the energy transfer to the Al complex part. Breaking the π-conjugation at the 8-quinolinol-5,7-diyl unit may be one of reasons for the slow energy transfer.

In the cast film, the main PL peak of polymer-4a(6/4-OEH) shifts to 536 nm. The large PL shift from 472 to 536 nm in going from the solution to the film is attributed to formation of an excimer-like adduct in the film. π-Conjugated polymers including the PAE-type polymers often show such a PL shift to a longer wavelength, and it has been assigned to the formation of the excimer-like adduct.[11] For polymer-6a(6/4-OEH−Al), the PL peak is also shifted to a longer wavelength as shown in Figure 6b. However, the degree of the shift is smaller than that observed with polymer-4a(6/4-OEH). In this case, the formation of the excimer-like adduct seems to be retarded because of twisting of the polymer main chain by incorporation of the bulky Al complex. The PL peak of polymer-6a(6/4-OEH−Al), at 507 nm agrees well with the PL peak of [Al(q′)$_2$(q)] **2**. These results suggest that the photoenergy captured by the polymer main chain is shifted to the Alq_3-type center formed in the polymer complex and the PL emission takes place from the Alq_3-type optical center.

By contrast, a simple mixture of polymer-4a(6/4-OEH) and [Al(q′)$_2$(q)] (1:1) showed only a broad PL peak at 557 nm in the film, and the PL peak from the Alq_3-type complex was not observed (cf. Figure S4 in Supporting Information). These results indicate that the effective transfer of the photoenergy captured by the polymer main chain to the Alq_3-type unit in polymer-6a(6/4-OEH−Al) takes place in the solid state, and the occurrence of interchain-type energy transfer of the photoenergy captured by the polymer main chain to the Al complex in the solid state is suggested. UV−vis and PL data of the polymer complexes are included in Table 2.

Conclusions

New main-chain-type 8-quinolinol polymers can be prepared via the Pd-catalyzed polycondensation. The 8-quinolinol polymer gave the Alq_3-type polymer complex, and the 8-quinolinol polymers and the Alq_3-type polymer complexes are photoluminescent with quantum yields of 15−49%. Main-chain-type 8-quinolinol polymers such as polymer-4a are expected to be the starting material for light emitting polymer complexes.

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Supporting Information Available: ^{1}H NMR data ($CDCl_3/\delta$) and yields of the polymers, XRD pattern of polymer-4a(6/4-OEH), effects of NaOH on light emission of polymer-4a(6/4-OEH) and polymer-4b(6/4-OEH), $^{13}C\{^1H\}$ NMR spectrum of the model compound **1**, and photoluminescence spectra of a mixture of polymer-4a(6/4-OEH) and [Al(q′)$_2$(q)] **2** (in a 1:1 molar ratio) in $CHCl_3$ and in cast film. This information is available free of charge via the Internet at http://pubs.acs.org.

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