Supporting Information

$^1$H NMR data (CDCl$_3$/δ) 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{$^1$H} NMR spectrum of the model compound 1. 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.

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

Takayuki Iijima, Shin-ichi Kuroda, and Takakazu Yamamoto*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan and Faculty of Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu-shi, Gunma, 376-8515, Japan
$^1$H NMR (CDCl$_3$ / $\delta$) data and yield of the polymers.

**polymer-1a(6/4-OC12)**, Yield: 79%. 8.82 (0.8H, 2-H-Q, 4-H-Q), 7.95 (0.4H, 6-H-Q), 7.47 (0.4H, 3-H-Q), 7.01 (3.2H, Ar-H), 4.09 (6.4H, -OCH$_2$), 1.86-1.25 (32H, CH$_2$), 1.13 (3.6H, tert-Bu), 0.87 (9.6H, -CH$_3$), 0.39 (2.4H, -Si(CH$_3$)$_2$).

**polymer-1b(6/4-OC12)**, Yield: 91%. 8.92 (0.4H, 2-H-Q), 8.19 (0.4H, 4-H-Q), 7.61 (0.4H, 5-H-Q), 7.27 (0.4H, 7-H-Q), 7.05 (3.2H, Ar-H), 4.03 (6.4H, -OCH$_2$), 1.86-1.25 (32H, CH$_2$), 1.07 (3.6H, tert-Bu), 0.85 (9.6H, -CH$_3$), 0.38 (2.4H, -Si(CH$_3$)$_2$).

**polymer-1c(6/4-OC12)**, Yield: 63%. 8.89 (0.4H, 2-H-Q), 8.20 (0.4H, 4-H-Q), 7.67 (0.4H, 5-H-Q), 7.21 (0.4H, 7-H-Q), 7.02 (3.2H, Ar-H), 4.01 (6.4H, -OCH$_2$), 1.86-1.25 (32H, CH$_2$), 1.12 (3.6H, tert-Bu), 0.86 (9.6H, -CH$_3$), 0.37 (2.4H, -Si(CH$_3$)$_2$).

**polymer-1a(8/2-OC12)**, Yield: 89%. 8.82 (0.4H, 2-H-Q, 4-H-Q), 7.94 (0.2H, 6-H-Q), 7.52 (0.2H, 3-H-Q), 7.01 (3.6H, Ar-H), 4.03 (7.2H, -OCH$_2$), 1.86-1.25 (36H, CH$_2$), 1.13 (1.8H, tert-Bu), 0.87 (10.8H, -CH$_3$), 0.39 (1.2H, -Si(CH$_3$)$_2$).

**polymer-1b(8/2-OC12)**, Yield: 91%. 8.91 (0.2H, 2-H-Q), 8.18 (0.2H, 4-H-Q), 7.58 (0.2H, 5-H-Q), 7.33 (0.2H, 7-H-Q), 7.01 (3.6H, Ar-H), 4.03 (7.2H, -OCH$_2$), 1.85-1.25 (36H, CH$_2$), 1.09 (1.8H, tert-Bu), 0.87 (10.8H, -CH$_3$), 0.30 (1.2H, -Si(CH$_3$)$_2$).

**polymer-1a(6/4-OCEH)**, Yield: 85%. 8.84 (0.4H, 2-H-Q), 8.77 (0.4H, 4-H-Q), 7.95 (0.4H, 6-H-Q), 7.53 (0.4H, 3-H-Q), 7.00 (3.2H, Ar-H), 3.91 (6.4H, -OCH$_2$), 1.82 (3.2H, -CH), 1.56-1.25 (32H, CH$_2$), 1.13 (3.6H, tert-Bu), 0.98, 0.89 (19.2H, -CH$_3$), 0.39 (2.4H, -Si(CH$_3$)$_2$).

**polymer-1b(6/4-OEH)**, Yield: 77%. 8.92 (0.4H, 2-H-Q), 8.17 (0.4H, 4-H-Q), 7.58 (0.4H, 5-H-Q), 7.46 (0.4H, 7-H-Q), 7.00 (3.2H, Ar-H), 3.91 (6.4H, -OCH$_2$), 1.82 (3.2H, -CH), 1.56-1.25 (32H, CH$_2$), 1.09 (3.6H, tert-Bu), 0.92, 0.89 (19.2H, -CH$_3$), 0.30 (2.4H, -Si(CH$_3$)$_2$).

**polymer-1a(8/2-OEH)**, Yield: 90%. 8.84 (0.2H, 2-H-Q), 8.74 (0.2H, 4-H-Q), 7.95 (0.2H, 6-H-Q), 7.49 (0.2H, 3-H-Q), 6.99 (3.6H, Ar-H), 3.98 (7.2H, -OCH$_2$), 1.82 (3.6H, -CH), 1.56-1.25 (36H, CH$_2$), 1.13 (1.8H, tert-Bu), 0.98, 0.89 (21.6H, -CH$_3$), 0.39 (1.2H, -Si(CH$_3$)$_2$).

**polymer-1b(8/2-OEH)**, Yield: 97%. 8.92 (0.2H, 2-H-Q), 8.16 (0.2H, 4-H-Q), 7.57 (0.2H, 5-H-Q), 7.52 (0.2H, 7-H-Q), 7.00 (3.6H, Ar-H), 3.91 (7.2H, -OCH$_2$), 1.82 (3.6H, -CH), 1.56-1.25 (36H, CH$_2$), 1.09 (1.8H, tert-Bu), 0.97, 0.88 (21.6H, -CH$_3$), 0.30 (1.2H, -Si(CH$_3$)$_2$).

**polymer-2a(6/4)**, Yield: 82%. 8.85 (0.4H, 2-H-Q), 8.68 (0.4H, 4-H-Q), 8.00 (0.4H, 6-H-Q), 7.70-7.51 (9.6H, Fl-H), 7.46 (0.4H, 3-H-Q), 2.00 (6.4H, -CH$_2$), 1.25-1.07 (32H, CH$_2$), 1.13 (3.6H, tert-Bu), 0.82 (9.6H, -CH$_3$), 0.62 (6.4H, -CH$_2$), 0.39 (2.4H, -CH$_2$).
-Si(CH$_3$)$_2$).

**polymer-2b(6/4)**, Yield: 83%. 8.97 (0.4H, 2-H-Q), 8.25 (0.4H, 4-H-Q), 7.70-7.51 (9.6H, Fl-H), 7.67 (0.4H, 5-H-Q), 7.33 (0.4H, 7-H-Q), 2.02 (6.4H, -CH$_2$), 1.25-1.07 (32H, CH$_2$), 1.18 (3.6H, tert-Bu), 0.82 (9.6H, -CH$_3$), 0.64 (6.4H, -CH$_2$), 0.32 (2.4H, -Si(CH$_3$)$_2$).

**polymer-2a(8/2)**, Yield: 78%. 8.85 (0.2H, 2-H-Q), 8.68 (0.2H, 4-H-Q), 8.00 (0.2H, 6-H-Q), (11H, Fl-H, 3-H-Q), 2.01 (7.2H, -CH$_2$), 1.25-1.07 (36H, CH$_2$), 1.13 (1.8H, tert-Bu), 0.82 (10.8H, -CH$_3$), 0.62 (7.2H, -CH$_2$), 0.40 (1.2H, -Si(CH$_3$)$_2$).

**polymer-2b(8/2)**, Yield: 74%. 8.97 (0.2H, 2-H-Q), 8.25 (0.2H, 4-H-Q), 7.70-7.51 (9.6H, Fl-H), 7.67 (0.2H, 5-H-Q), 7.33 (0.2H, 7-H-Q), 2.02 (7.2H, -CH$_2$), 1.25-1.07 (36H, CH$_2$), 1.18 (1.8H, tert-Bu), 0.82 (10.8H, -CH$_3$), 0.64 (7.2H, -CH$_2$), 0.32 (1.2H, -Si(CH$_3$)$_2$).

**polymer-3**, Yield: 97%. 9.02 (0.4H, 2-H-Q), 8.82 (0.4H, 4-H-Q), 7.88 (0.4H, 6-H-Q), 7.53 (0.4H, 3-H-Q), 7.01 (3.2H, Ar-H), 4.50 (1.2H, -OCH$_3$), 4.03 (6.4H, -OCH$_2$), 1.86-1.25 (32H, CH$_2$), 0.87 (9.6H, -CH$_3$).

**polymer-4a(8/2-OC12)**, Yield: 100%. 8.84 (0.4H, 2-H-Q, 4-H-Q), 7.91 (0.2H, 6-H-Q), 7.52 (0.2H, 3-H-Q), 7.01 (3.6H, Ar-H), 4.03 (7.2H, -OCH$_2$), 1.86-1.25 (36H, CH$_2$), 0.87 (10.8H, -CH$_3$).

**polymer-4b(8/2-OC12)**, Yield: 96%. 8.85 (0.2H, 2-H-Q), 8.23 (0.2H, 4-H-Q), 7.67 (0.2H, 5-H-Q), 7.27 (0.2H, 7-H-Q), 7.01 (3.6H, Ar-H), 4.03 (7.2H, -OCH$_2$), 1.86-1.25 (36H, CH$_2$), 0.87 (10.8H, -CH$_3$).

**polymer-4a(6/4-OEH)**, Yield: 81%. 8.84 (0.4H, 2-H-Q), 8.78 (0.4H, 4-H-Q), 7.92 (0.4H, 6-H-Q), 7.53 (0.4H, 3-H-Q), 7.00 (3.2H, Ar-H), 3.91 (6.4H, -OCH$_2$), 1.82 (3.2H –CH), 1.56-1.25 (38.4H, CH$_2$), 0.96, 0.88 (19.2H, -CH$_3$).

**polymer-4b(6/4-OEH)**, Yield: 86%. 8.84 (0.4H, 2-H-Q), 8.22 (0.4H, 4-H-Q), 8.05 (0.4H, OH), 7.52 (0.4H, 5-H-Q), 7.27 (0.4H, 7-H-Q), 7.00 (3.2H, Ar-H), 3.91 (6.4H, -OCH$_2$), 1.81 (3.2H –CH), 1.56-1.25 (38.4H, CH$_2$), 0.98, 0.88 (19.2H, -CH$_3$).

Anal. Found: C, 78.84; H 8.85; N, 0.93; Br, 1.68; C/N atomic ratio = 98.9. The following molecular structure roughly agrees with the found values. Calcd for the following molecular structure: C, 79.19; H, 9.20; N, 0.97; Br, 1.73; C/N atomic ratio = 94.9.

![Chart S1](image)

**Chart S1  Postulated Molecular Structure of polymer-4b(6/4-OEH)**

The PAE-type polymer synthesized by the Pd-catalyzed polycondensation has a
halogenated terminal group as the main terminal group. The above shown molecular structure gives $M_n$ of 9260. The $M_n$ corresponds $M_n$ of 9260 + (molecular weight of the $-\text{SiMe}_2\text{tBu}$ group) $\times$ 6.43 = 10000 of original polymer-$1b(6/4$-OEH), which roughly agrees with the observed $M_n$ (10400) of polymer-$1b(6/4$-OEH). The above shown molecular structure somewhat deviates from the feeding ratio between monomer-$4$ and monomer-$b$ and indicates that monomer-$4$ had somewhat higher reactivity than monomer-$b$. The relative reactivity ratio between monomer-$4$ and monomer-$b$ is calculated as $8/6 : 6/4 = 1 : 1.13$.

**Reaction with [Al(Et)(q')$_2$]** After the reaction with [Al(Et)(q')$_2$], the above shown C/N atomic ratio (98.9) of polymer-$4b(6/4$-OEH) decreased to (59.3), which corresponds to transformation of about 30% of the 8-quinolinol unit to the Al complex. If two of the 6.43 8-quinolinol units in the polymer shown in Chart S1 react with [Al(Et)(q')$_2$], the degree of the transformation is about 30% (= 2/6.43) and the C/N atomic ratio becomes 62.4. Determination of the C/N ratio and C/Al ratio by ESCA (electron spectroscopy for chemical analysis) was not possible due to low content of N and Al in the polymer.

**polymer-$4a(8/2$-OEH)**, Yield: 88%. 8.81 (0.2H, 2-H-Q), 8.78 (0.2H, 4-H-Q), 7.91 (0.2H, 6-H-Q), 7.53 (0.2H, 3-H-Q), 6.99 (3.6H, Ar-H), 3.90 (7.2H, -OCH$_2$), 1.81 (3.6H –CH), 1.63-1.25 (43.2H, CH$_2$), 0.98, 0.88 (19.2H, -CH$_3$).

**polymer-$4b(8/2$-OEH)**, Yield: 92%. 8.84 (0.2H, 2-H-Q), 8.21 (0.2H, 4-H-Q), 8.05 (0.2H, OH), 7.51 (0.2H, 5-H-Q), 7.27 (0.2H, 7-H-Q), 6.99 (3.6H, Ar-H), 3.90 (7.2H, -OCH$_2$), 1.81 (3.6H –CH), 1.56-1.25 (43.2H, CH$_2$), 0.98, 0.88 (19.2H, -CH$_3$).
Figure S1  Powder XRD pattern of polymer-4a(6/4-OEH).
Figure S2. Emission of light from polymer-4a(6/4-OEH) and polymer-4b(6/4-OEH) in the presence of NaOH in a 4:1 (v/v) mixed THF-methanol solution. (a) polymer-4a(6/4-OEH), (b) polymer-4a(6/4-OEH) with NaOH, (c) polymer-4b(6/4-OEH), and (d) polymer-4b(6/4-OEH) with NaOH. This photograph was taken under irradiation with light at 365 nm. N$_2$ was bubbled in the solution and the sample tube was sealed.
**Figure S3.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the model compound 1 in CDCl$_3$. The peak with a * is due to solvent impurity (CDCl$_3$).
**Figure S4.** Photoluminescence spectra of a mixture of polymer-4a(6/4-OEH) and [Al(q')2(q)] 2 (in a 1 :1 molar ratio) in CHCl₃ (solid line) and in cast film (dashed line).