

Synthesis of the Platinum Diketonate-Containing Polymer Having Oxygen-Resistant Phosphorescence

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KEYWORDS

platinum complex, diketonate, oxygen, conjugated polymer

ABSTRACT

We report the synthesis of the platinum diketonate-based alternating copolymer composed of the fluorene unit and its oxygen-resistant phosphorescence. The polymerization was executed via the palladium-catalyzed Suzuki–Miyaura coupling reaction. The synthesized polymer showed good solubility in common organic solvents and processability to form homogeneous films. From the optical measurements, it was found that the synthesized polymer showed a phosphorescence from a triplet $\pi\text{-}\pi^*$ ligand-centered transition. Interestingly, these emission behaviors were hardly influenced by oxygen. Consequently, it was revealed that the phosphorescence was observed from both solution and film samples under aerobic conditions. The new idea for obtaining emissive materials based on the conjugated polymers having the oxygen-resistant phosphorescence is presented here.

Introduction

The development of new conjugated polymers is a topic with high relevance because of a wide versatility of the polymeric materials not only for saving the fabrication cost on the device processing with the printing method but also for obtaining advanced organic opto and/or electro devices. Various unique structures as a functional unit have been conjugated into the polymer main-chain, and interesting characteristics were obtained. In the electroluminescence (EL) devices, 75% of the excitons are promised to form the triplet state via spin-dependent charge recombination. Thereby, the phosphorescent chromophores are advantageous as an emissive material for improving device efficiency.¹ In particular, the polymeric materials with phosphorescent properties are strongly required for fabricating highly-efficient EL devices.² Furthermore, in the design of optical bioprobes, phosphorescent materials are advantageous. Fraser *et al.* have accomplished to monitor the oxygen concentrations in the tumor regions utilizing the ratiometric bioprobes with the dual emission property.³ The local oxygen concentration was estimated by calculating the emission ratios between fluorescence and phosphorescence from the probes. In addition, since the emission lifetime of phosphorescence is relatively longer than that of fluorescence, it is possible to have the time lag between the acquisition starting time and the excitation moment with the probe molecules.⁴ The background noise caused from the intrinsic autofluorescence can be effectively eliminated at the detection by delaying the acquisition timing of the image capturing. However, phosphorescence is inevitably quenched by oxygen.^{5,6} Based on this sensitivity, various types of oxygen sensors have been developed with polymeric materials.⁵ The amount of oxygen in the air and solvents can be monitored quantitatively.⁵ As another instance, the Pt-diketonate-containing conjugated polymer showed a quenching of approximately 30–40% of the phosphorescence emission in the solution by the dissolved air.⁶ In these materials, the improvement of the sensitivity is focused for the precise detection of oxygen. Thus, the development of the polymers having oxygen-resistant phosphorescence is still challenging and is of significance particularly for improving the efficiency of EL devices.

Fluorene is one of the widely-used monomer units for preparing the optically- and/or electrically-functional materials. Polyfluorenes and fluorene-based polymers work as a photo-antenna, resulting in highly-bright emission system.⁷ By introducing the functional groups at the 9-position of fluorene, the suppression of the concentration-quenching and the improvement of the film-formability have been achieved.⁸ Fluorene-containing alternating copolymers are also versatile. By selecting a type of comonomers, various electronic functionalities can be expressed. In the previous reports, there are several examples to offer the conjugated molecules based on fluorene with the organometallic compounds. By employing diketonates and their analogues which are capable to form a complex with a wide variety of metal species, functional polymeric materials have been developed.⁹ For example, boron diketonate-containing polymers can show the strong emissions.¹⁰ By tuning the complexation ratio in the polymer main-chain, the color tuning in the visible light region was demonstrated.¹¹ Although the versatility of organometallic diketonates is much higher, the limited number of the researches on the direct conjugation with fluorene and platinum complex was accomplished. Since there is a large possibility to realize further functions originated from the combination of fluorene and platinum complexes in the conjugation systems, the construction of the main-chain type polymers containing the direct connecting unit between fluorene and the platinum diketonates is of significance.

Herein, we report the synthesis of fluorene alternating copolymers containing platinum diketonate in the main-chain. From the evaluation of optical properties, we found the phosphorescence originated from the platinum complex. Interestingly, it was revealed that the phosphorescent behaviors were protected from oxygen which is normally the critical quencher toward phosphorescence emissions. Finally, we observed the phosphorescence from both of the polymer solutions and films under aerobic conditions.

Results and discussion

We preliminary carried out an introduction of platinum element into the ligand in the polymers via the polymer reaction. However, the complexation ratio was too low, and the desired polymers were not completely obtained. Therefore, alternatively the polymerization was performed with the platinum complexes-containing monomer. The ligand **1** was prepared according to our previous report.¹² The introduction of platinum to the diketonate units was executed with Pt dimer prepared based on the Swager's method.⁶ It is known that the steric hindrance by the alkyl substituent at the 9-position in fluorene critically reduces the reaction yield of the formation of a diketonate structure and the polymerization. To maintain the solubility, n-octyl- and 2-ethylhexyl-substituted fluorenes were alternatively used as monomers (Scheme 1). Diiodide monomer **2** was characterized by ¹H and ¹³C NMR spectroscopies and mass measurements to confirm the chemical structure.

Scheme 1

The polymerization with diiodide monomers via Suzuki–Miyaura coupling was executed as shown in Scheme 1. When the n-octyl groups-substituted comonomer was used, the polymeric products were hardly obtained because of the aggregation formation. Thus, we used the 2-ethylhexyl-substituted comonomer was applied. The polymer properties were determined from the GPC analysis. To completely remove the metal species used as the catalyst in the polymerization, the reprecipitation and washing with methanol were executed. The number-average molecular weights (M_n) and the molecular weight distributions of the polymers (M_w/M_n), measured by the size-exclusion chromatography in chloroform toward polystyrene standards were 8,200 and 1.35, respectively, so whether we apply the M_w of the repeating unit **P1** (~1,700), or even if we use the M_w of a repeating unit bearing one Pt (~900), the DP is less than 10. So, one could label this material as almost oligomer-like. On the other hand, by elongating the polymer chain, it was observed that the solubility of the products critically decreased, leading to the lowering of the isolation

yields and the loss of film-formability. Therefore, we used the oligomer in this study. Consequently, the products were solved in common organic solvents such as chloroform and THF. The data for structural analysis by ^1H and ^{13}C NMR were corresponded to those of the monomer and model compounds. Thus, we concluded that the polymers should possess the expected chemical structures.

The electronic structures of the polymer at the ground state were examined by UV-vis absorption in the chloroform solution and in the film state (Figure 1). The results are summarized in Table 1. The absorption band with the peak at 387 nm was observed from the solution sample. Interestingly, the similar shape of the spectrum was observed from the film sample, too. The peak position of the absorption band was found around the same position ($\lambda_{\text{max}} = 392$ nm). In the previous reports, conjugated polymers composed of fluorene-based alternating polymers showed the bathochromic shifts (> 10 nm) in the film state comparing to the solution state because of the interchain stacking or aggregation formation.¹³ The peak shift of the absorption band within 5 nm was observed even in the higher concentrated solution in this experiment. These data mean that electronic interactions should be disturbed even in the condensed state. The steric hindrance of the alkyl substitutions at the fluorene units could contribute to isolating the polymer main-chains.

Figure 1 and Table 1

Next, the electronic structures of the polymers at the excited states were examined from the emission measurements (Figure 2). From both of the solution and film samples, the significant emissions were observed. In the chloroform solution, the polymer provided the emission band with the peak at 538 nm. It should be mentioned that the emission spectrum with the film was recorded in the open air. In contrast to the solution state, the broad emission band with the peak around 582 nm was observed from the polymer film. The emission lifetime of the polymer solution was determined as $0.36 \mu\text{s}$. Comparing to the lifetimes of the common fluorescent polymers such as polyfluorenes and boron ketoiminate-containing polymers

(several ns order), longer values were obtained from the platinum complex-containing polymer.^{7,8} These data indicate that the emission from the polymer is attributable to phosphorescence. From the film sample, the decay time was shortened to 0.12 μ s. Another decay pass in the faster time region was detected (0.024 μ s) with a relatively-large proportion (39%). These data suggest that the electronic interactions between the polymer chains should occur at the excited state. The decrease of the emission quantum yield in the film state also implies the existence of the interaction.

Figure 2

To understand the emission mechanism of the polymer, further experiments were performed. According to the previous reports on the optical properties of the monomer unit, the emission band of the platinum complex was assigned as a phosphorescence from a triplet $\pi-\pi^*$ ligand-centered (3 LC) transition.^{12,14} To evaluate this mechanism, the solvent dependency of the peak position of the emission was initially monitored. From the experimental results, the Lippert–Mataga plots were prepared (Figure 3). Obviously, less solvent dependency was observed compared to boron diketonate which showed a CT emission.¹² Furthermore, the red shift of the emission band obtained at 77 K was slightly observed comparing to the spectrum recorded at ambient temperature (Figure 2b). These data mean that the emission should be attributable not to a triplet metal-to-ligand CT transition but to a 3 LC transition.¹⁴ From these data, it is concluded that the synthesized polymer shows a phosphorescence from a 3 LC transition.

Figure 3

In general, phosphorescence is critically quenched by the interaction with oxygen.^{5,6} Therefore, at the surface of emissive devices based on phosphorescent dyes, strict shielding from oxygen should be essential. We investigated the influence of the dissolved oxygen level on the emission of the polymers.

The emission intensities were compared with the solution samples with the argon- and oxygen-bubbling treatments until the saturation (at least 11.6 mmol/L) under ambient condition (Figure 4).¹⁵ With the same sample, the bubbling treatments were executed, and the change in the emission spectrum was pursued. Notably, the emission intensity was hardly changed even after the oxygen bubbling. Comparing to the concentration in water (ca. 1.4 mmol/L),¹⁵ the much larger amount of oxygen can be dissolved into chloroform.⁵ In addition, although the decrease of the phosphorescence emission by 30–40% was observed from the polymer composed of the platinum complex with the different conjugation motif, our polymer showed similar level of phosphorescence.⁶ This result is the direct evidence that the synthesized polymer can show the oxygen-resistant phosphorescence. In the previous report with the monomer unit, the low dependency of the phosphorescence intensity on the dissolved oxygen level was observed in the solution state.¹² It is suggested that the steric hindrance could disturb the access of oxygen molecules, resulting in the unchanged phosphorescence from the polymer.^{5a,16} Including the emission behaviors of the film sample in the open air, it can be said that the synthesized polymer should have the oxygen-resistant phosphorescence.

Figure 4

Conclusion

We present the synthesis and oxygen-resistant phosphorescence of platinum diketonate-based alternating copolymers. This study involves two significant issues: The direct connection between fluorene and platinum diketonate in the polymer main-chain was established by employing the Suzuki–Miyaura cross-coupling reaction. The polymeric products showed good solubility in common organic solvents and processability for the preparation of homogeneous films. In particular, the synthesized polymer possesses the conjugation system through the main-chain, which is a key for expressing optoelectric functions in the devices. Secondly, the robust oxygen-resistant phosphorescence was observed from the products. Owing to the neighbor alkyl chains, the preservation of phosphorescence from the oxygen quenching could be obtained. Our findings could be applicable directly not only for improving the efficiency of the polymer-based EL devices but also for constructing advanced bioprobes using the advantages of phosphorescence with the independency from the oxygen concentration.

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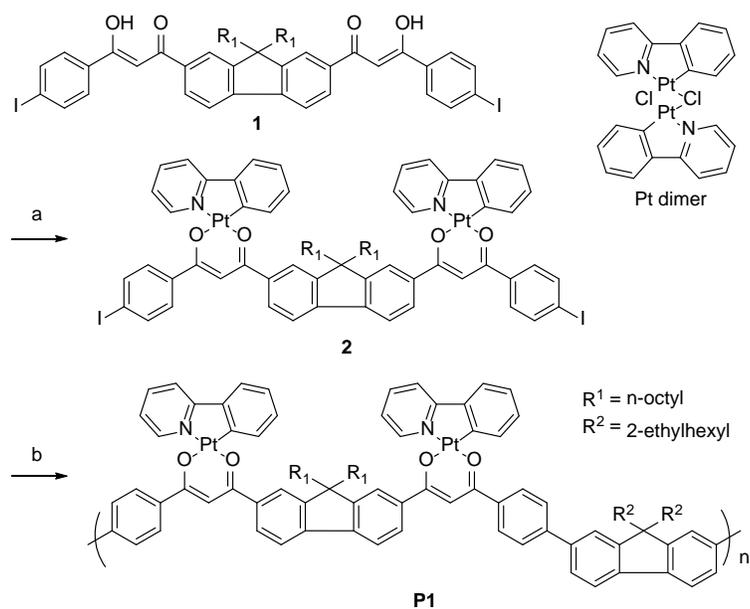
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Table and Figures

Scheme 1. Synthetic scheme of a monomer and a polymer^a



^aReagents and conditions: (a) Pt dimer, Na₂CO₃, 2-ethoxyethanol, 100 °C, 24 h; (b) [9,9-Bis(2-ethylhexyl)-9H-fluorene-2,7-diyl]bisboronic acid, S-Phos, Pd₂(dba)₃, Cs₂CO₃, toluene, water, 80 °C, 7 d.

Table 1. Photophysical properties of the polymer

	$\lambda_{\text{abs,max}}$ (nm)	$\lambda_{\text{em,max}}$ (nm)	Φ^b	τ (μs)
Solution ^a	387	538	0.01	0.36
Film	392	582	<0.01	0.12 (61%), 0.024 (39%)
Glassy state ^{a,c}		552		1.2×10^3

^a Measured in the chloroform solution (1.0×10^{-5} M). ^b Absolute quantum yield. ^c Measured in 2-methyl-THF at 77 K.

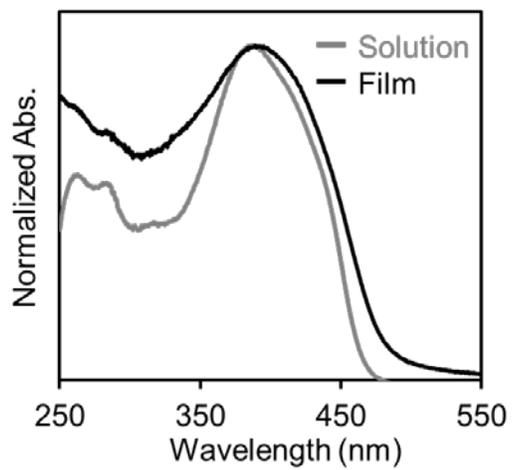


Figure 1. UV-vis spectra of the polymer in the chloroform solution (1.0×10^{-5} M, gray line) and in the film (black line).

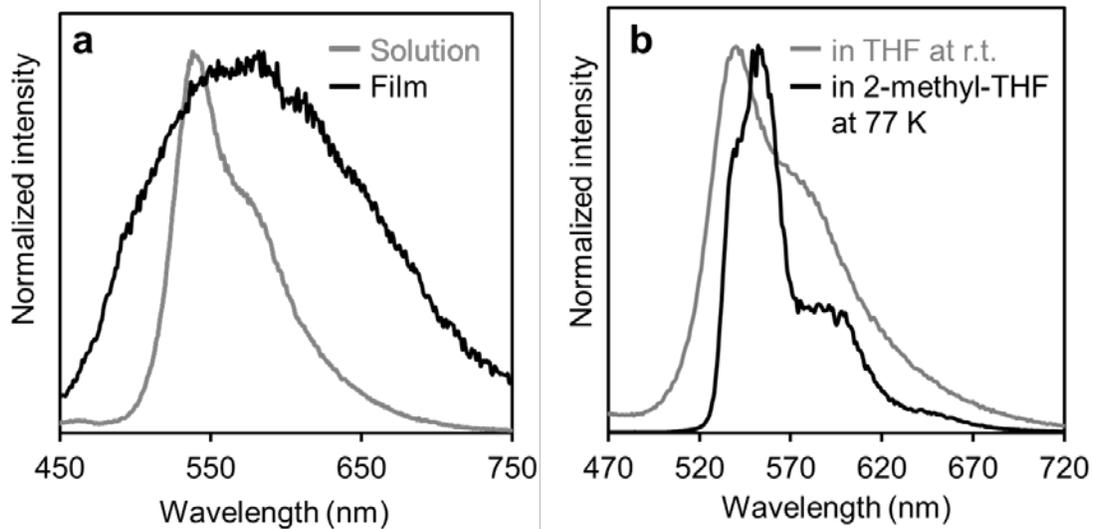


Figure 2. (a) Emission spectra of the polymer in the chloroform solution (1.0×10^{-5} M, gray line) and in the film state (black line). (b) Emission spectra of the polymer solutions of THF at r.t. (gray line) and 2-methyl-THF at 77 K (black line).

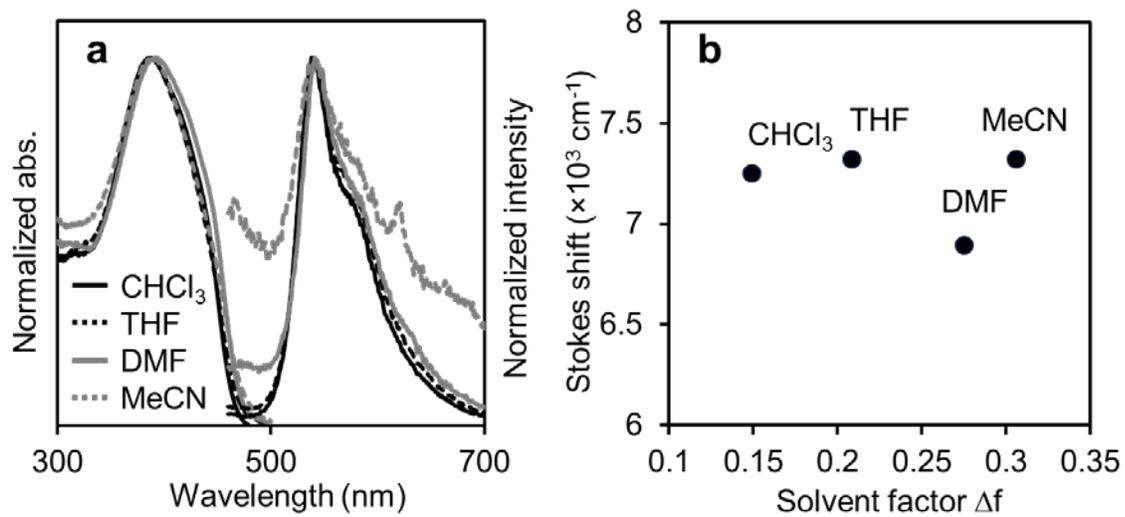


Figure 3. (a) Emission spectra of the polymer in various solvents. (b) Lippert–Mataga plots of the polymer. The solvent function Δf was defined in eq 2 for a series of various solvents.

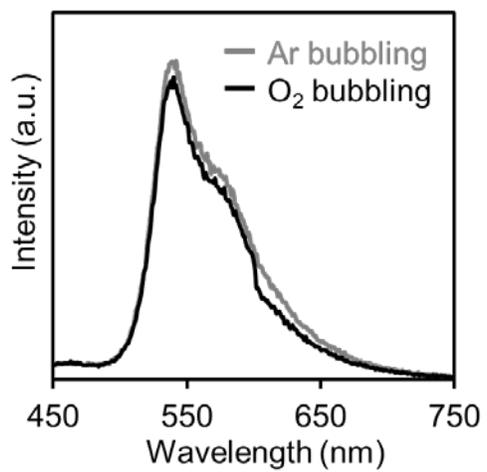
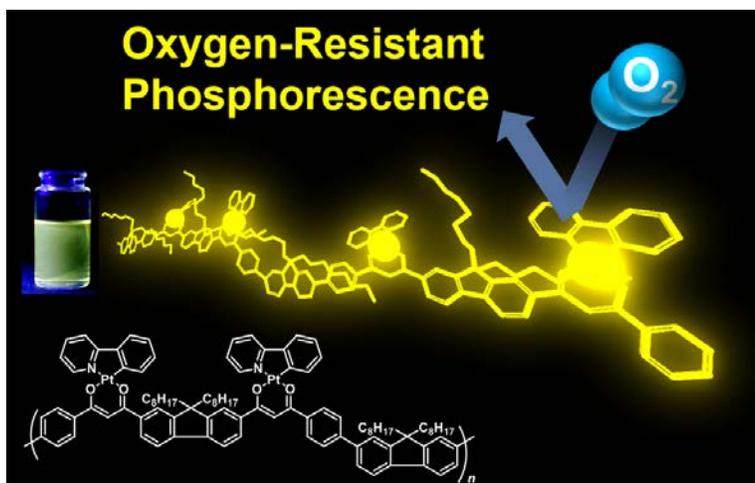


Figure 4. (a) Emission spectra of the polymer in the chloroform solution after argon (gray line) and oxygen (black line) bubbling.

Graphical abstract



Supporting Information

Synthesis of the Platinum Diketonate-Containing Polymer Having Oxygen-

Resistant Phosphorescence

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Experimental section

General. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on JEOL JNM-EX400 spectrometers. ^1H NMR spectra used tetramethylsilane (TMS) as an internal standard in CDCl_3 , and ^{13}C NMR spectra used tetrahydrofuran as an internal standard in $\text{THF-}d_8$. The number-average molecular weight (M_n) and the molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] values of all polymers were estimated by the size-exclusion chromatography (SEC) with a TOSOH G3000HXL system equipped with three consecutive polystyrene gel columns (TOSOH gels: α -4000, α -3000, and α -2500) and ultraviolet detector at 40 °C. The system was operated at a flow rate of 1.0 mL/min, with chloroform as an eluent. Polystyrene standards were employed for the calibration. Recyclable preparative high-performance liquid chromatography (HPLC) was carried out on a Japan Analytical Industry Model LC918R (JAIGEL-1H and 2H columns) and LC9204 (JAIGEL-2.5H and 3H columns) using chloroform as an eluent. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer, and absolute quantum yields were determined by the integrating sphere method on the HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer in chloroform. Photoluminescence (PL) lifetime was measured by a

Horiba FluoreCube spectrofluorometer system and excitation was carried out at 375nm using UV diode laser (NanoLED 375 nm).

Materials. 2,7-Dibromo-9,9-di-*n*-octylfluorene and Pd₂(dba)₃ (dba = dibenzylideneacetone) were purchased from Tokyo Chemical Industry CO.,LTD. (Tokyo, Japan). 4'-Iodoacetophenone, NaH (sodium hydride) in mineral oil (50~72%), S-Phos (2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl), Cs₂CO₃, 2-phenylpyridine, K₂[PtCl₄] and Na₂CO₃ were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). *n*-BuLi in *n*-hexane (1.6 mol/L) was purchased from Kanto Chemical, CO.,INC. (Tokyo, Japan). [9,9-Bis(2-ethylhexyl)-9*H*-fluorene-2,7-diyl]bisboronic acid was purchased from SIGMA-ALDRICH, Co.. All solvents were used as a deoxidized grade. All chemicals and solvents were used as received without further purification. The diketonate ligand **1** and Pt dimer were synthesized according to the previous works.¹⁻³

Synthesis of monomer 2. In a round bottom flask with a drop funnel, **1**² (0.66 g, 0.71 mmol), Pt dimer³ (0.65 g, 0.85 mmol) and K₂CO₃ (0.75 mg, 7.1 mmol) were placed under nitrogen atmosphere, and degassed 2-ethoxyethanol (15 mL) was added to the flask. The reaction mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the

products were extracted with CH₂Cl₂. The organic layer was dried over magnesium sulfate and concentrated by a rotary evaporator. The crude product was suspended onto silica gel and purified by the silica gel column chromatography with a mixed eluent containing *n*-hexane/CHCl₃ (1:1). Monomer **2** was separated with HPLC in chloroform and precipitated in *n*-hexane. The pure **2** was obtained (150 mg, 13%) as a gray solid. ¹H NMR (CD₂Cl₂, ppm) δ 9.22 (1H, d, *J* = 4.9 Hz), 9.13 (1H, d, *J* = 5.1 Hz), 8.18–8.15 (5H, m), 7.94–7.93 (10H, m), 7.77–7.70 (4H, m), 7.58 (3H, d, *J* = 7.1 Hz), 7.31–7.19 (5H, m), 6.95 (1H, s), 6.89 (1H, s), 6.88 (1H, s), 2.22–2.15 (4H, m), 1.55 (2H, s), 1.16–1.14 (19H, m), 0.80 (9H, t, *J* = 6.7 Hz). ¹³C NMR (CD₂Cl₂, ppm) δ 181.14, 180.14, 179.24, 178.09, 169.19, 169.14, 153.01, 148.14, 148.09, 148.02, 145.84, 144.31, 144.22, 144.07, 143.98, 143.95, 143.84, 140.46, 140.39, 140.29, 140.08, 139.98, 139.73, 139.71, 139.65, 139.59, 139.56, 139.42, 138.77, 131.54, 130.03, 129.49, 129.46, 127.90, 127.87, 127.42, 127.22, 124.62, 124.59, 124.00, 122.79, 122.53, 122.47, 122.42, 121.38, 121.36, 121.26, 121.23, 119.52, 98.59, 98.38, 98.15, 98.07, 56.35, 41.08, 32.60, 30.98, 30.94, 30.12, 24.88, 23.42, 14.65. MALDI-TOF-MS (Matrix: DIT): calcd for [C₆₉H₆₆N₂O₄Pt₂+H]⁺: *m/z* 1631.2493; found: *m/z* 1631.2494.

Synthesis of P1. A mixture containing **2** (131 mg, 80.3 μmol), [9,9-bis(2-ethylhexyl)-9H-fluorene-2,7-diyl]bisboronic acid (38.4 mg, 80.3 μmol), S-Phos (1.3 mg, 3.2 μmol), $\text{Pd}_2(\text{dba})_3$ (0.7 mg, 0.8 μmol), and Cs_2CO_3 (262 mg, 803 μmol) in toluene (0.8 mL) and water (0.8 mL) was stirred at 80 °C for 7 d under argon atmosphere. After cooling to the room temperature, the reaction mixture was poured into an excess amount of methanol to collect the polymer by filtration. The precipitate was washed by water and ethanol. The precipitate was dissolved in a small amount of THF, and then the product was reprecipitated from methanol. The polymer was separated by recyclable preparative HPLC using CHCl_3 as an eluent to obtain **P1** as a gray solid (30 mg, 21%). ^1H NMR (CD_2Cl_2 , ppm) δ 9.1 (1H, br s), 8.3–6.8 (37H, br m), 2.1 (6H, br s), 1.2–0.4 (62H, br m) ppm. ^{13}C NMR (CD_2Cl_2 , ppm) δ 180.31, 179.54, 179.22, 178.42, 168.73, 152.52, 152.09, 151.74, 147.70, 147.59, 145.42, 144.70, 144.49, 143.80, 143.72, 143.56, 143.47, 143.28, 143.19, 141.22, 140.02, 139.56, 139.24, 139.14, 138.95, 138.14, 131.15, 129.60, 129.09, 129.06, 127.99, 127.65, 127.44, 127.40, 127.19, 126.93, 126.76, 126.57, 126.34, 124.64, 124.07, 123.54, 123.35, 123.26, 123.15, 122.33, 122.04, 120.84, 120.70, 120.37, 120.13, 119.09, 97.79, 55.90, 55.64, 55.41, 44.82, 40.69, 35.23, 35.10, 35.05, 34.26, 34.11, 32.14, 30.50, 29.83, 29.67, 28.63, 28.59, 28.51, 27.54, 27.51, 27.43, 27.26, 27.24, 24.42, 23.14, 23.05, 22.97, 14.21, 14.13, 10.58, 10.54, 10.48, 10.47, 10.42, 10.40.

Lippert–Mataga plots.¹ The Lippert equation:

$$\nu_{\text{fl}} = \nu_{\text{ab}} - \frac{2\Delta f}{hca^3} (\mu_{\text{E}} - \mu_{\text{G}})^2 + \text{const.} \quad (1)$$

where h equals Planck's Constant, c equals the velocity of light in a vacuum, a is the Onsager cavity radius, n and ε the refractive index and the dielectric constant of the solvent, ν_{fl} and ν_{ab} the fluorescence and absorption wavelength (expressed in cm^{-1} units), μ_{E} and μ_{G} the dipole moment (expressed in Debye units) in the excited and the ground state, respectively,

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{4n^2 + 2} \quad (2)$$

While the slope is

$$\text{Slope} = -\frac{2\Delta f}{hca^3} (\mu_{\text{E}} - \mu_{\text{G}})^2 \quad (3)$$

Based on the calculation performed above, we can estimate that the excited state of dyes has a larger dipole moment than the ground state.

References

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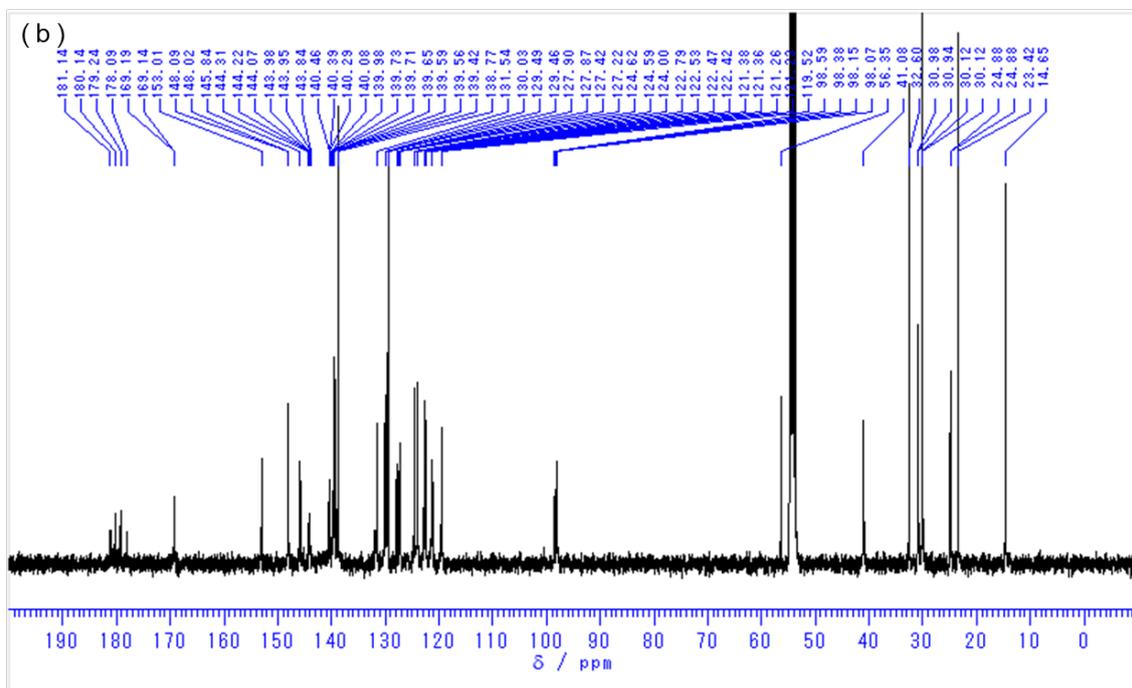
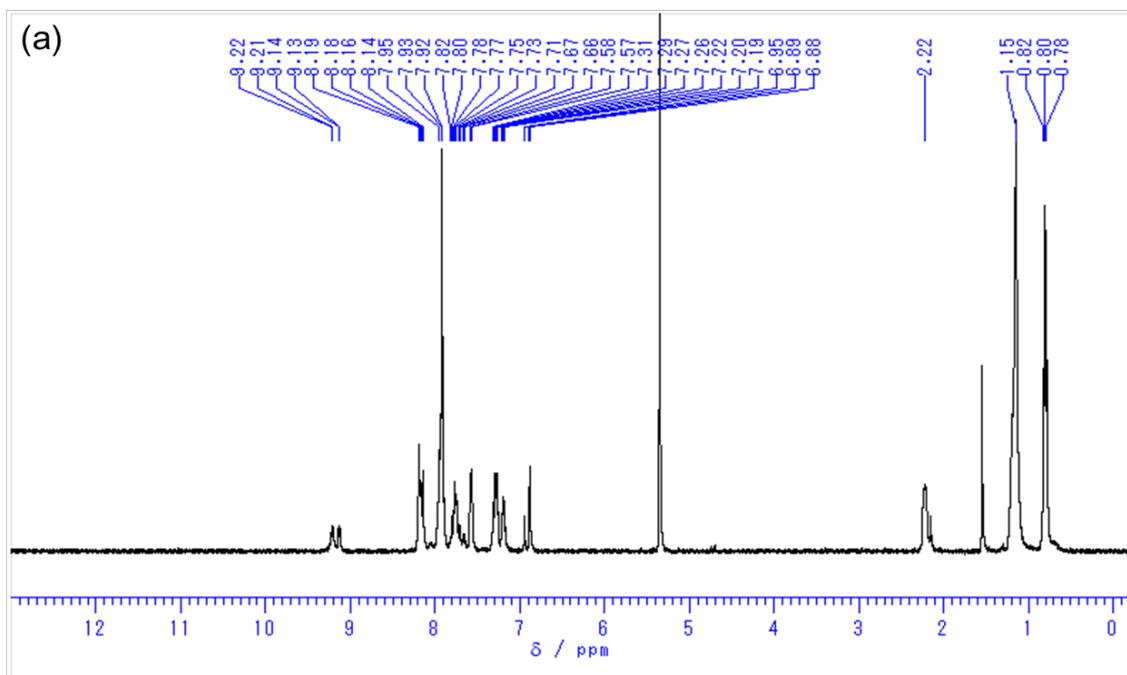


Figure S1. a) ^1H NMR and b) ^{13}C NMR spectra of **2** in CD_2Cl_2 .

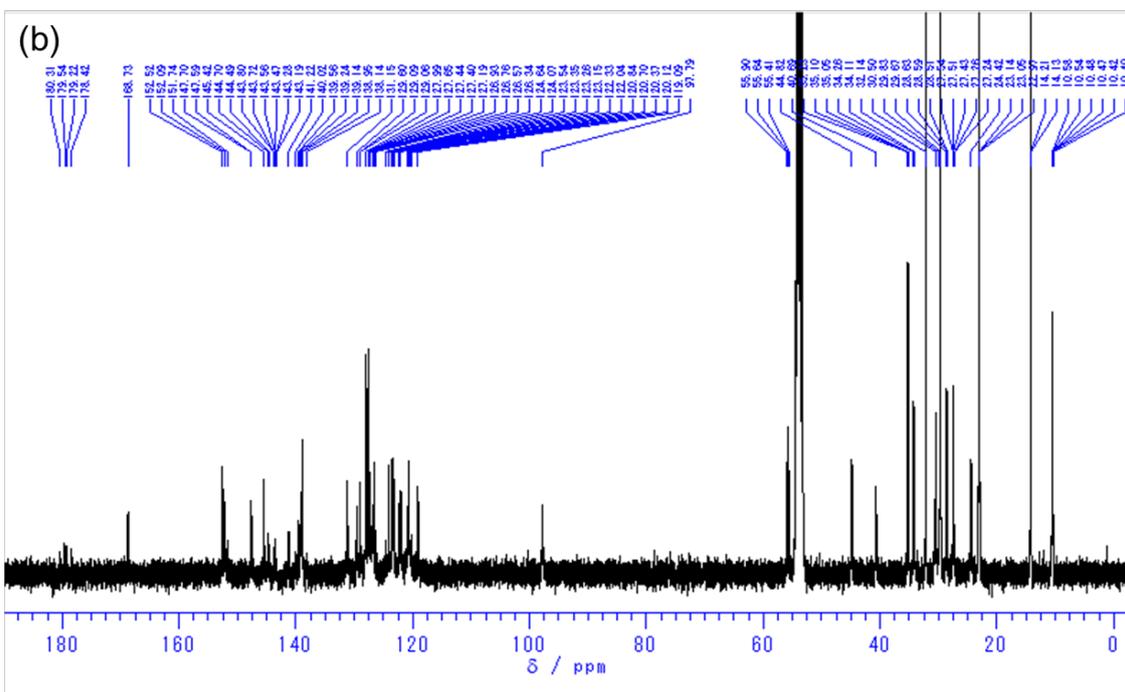
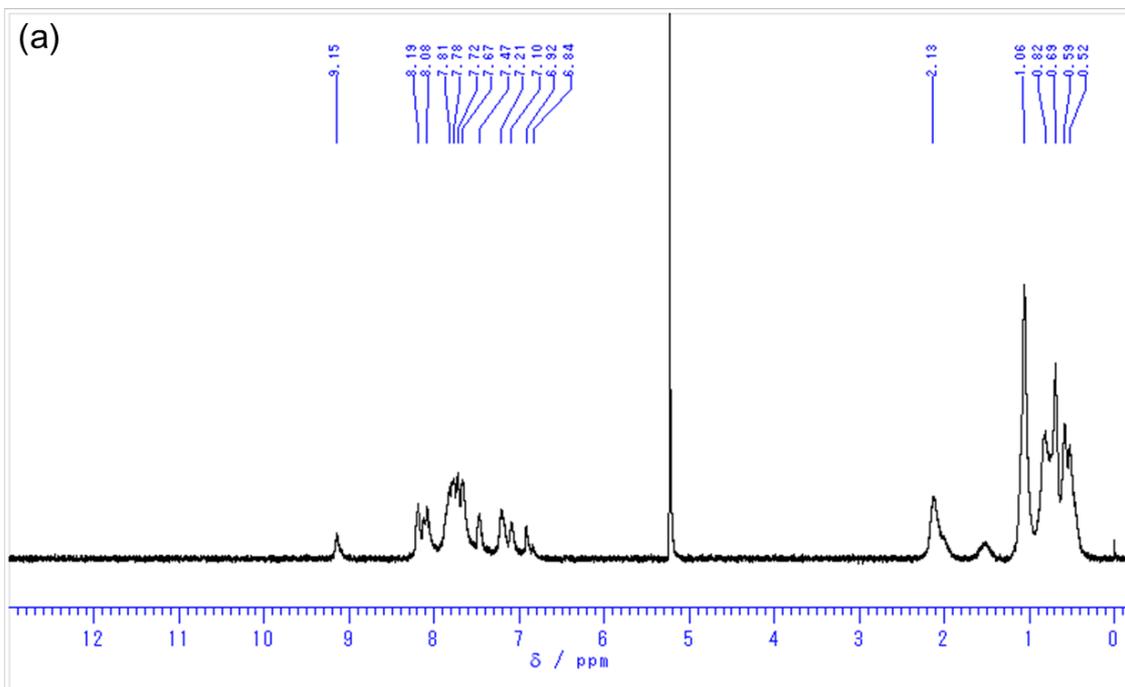


Figure S2. a) ^1H NMR and b) ^{13}C NMR spectra of **P1** in CD_2Cl_2 .