Synthesis of Tropolone-Containing Conjugated Polymers and Their Optical Properties

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ABSTRACT: A novel dibromo methyltropolone monomer (an isomeric mixture) was synthesized by the nucleophilic reaction to 2,4,7-tribromotropone. Methyltropolone-containing conjugated polymers were successfully obtained by Suzuki coupling, Mizoroguchi-Heck, and Sonogashira coupling reactions. The C=O stretching vibration signals shifted to the lower frequency region as compared with a monomer. The conversion from the methoxy group to the hydroxyl group was performed by the polymer reaction using LiI or BBr₃. The soluble conjugated polymers could be obtained from those bearing 9,9-dihexyl-2,7-fluorenylidene and 2,5-didecyl-1,4-phenylene segments. The formation of an intramolecular hydrogen bond was confirmed by the shift of the C=O vibration signal to the lower frequency region. In the UV and PL spectra, the maximum wavelengths were dependent upon the chemical structure of linkage and the presence of donor-acceptor interaction. The formation of an intramolecular hydrogen bond brought about the red shift of the absorption spectra and the quench of the fluorescence emission. [doi:10.1295/polymj.PJ2007003]

KEY WORDS Tropolone / Conjugated Polymer / Hydrogen Bond / Optical Properties /

Since conjugated polymers and oligomers have been attracted increasing attention for the application to light-emitting diodes, plastic lasers, and sensors, those with a novel structure were successively produced for the past decade. However, the relation between the device performance and the material structure is still a subject of discussion. Thus the fine control and tuning of optical properties of conjugated polymers are important topic to obtain photonic devices composed of these photoactive polymer materials.¹ The chemical modification of the polymer repeating unit is the direct method to modulate the effective conjugation length, which eventually influences the macromolecular optoelectronic properties such as emissive color, fluorescence quantum yield, and redox potential. In most of conjugated polymers, 5 and 6-membered aromatic rings with the 6 π electron system like benzene, thiophene, pyridine, and 1,3-oxazole are the component of the main chain. To gain further insight into the fundamental photophysics of conjugated polymers and to develop novel functional materials made from these polymers, the production of polymers having the segment with much different electronic character might be one of the challenging effort.²

Recently, we have reported the synthesis of a series of tropolone-containing conjugated polymers.³ The photophysical properties of polymer were strongly dependent upon the chemical structure of tropone unit. For example, the absorption maximum wavelength of a *p*-phenylenevinylene polymer containing tropone was observed at 515 nm, which dramatically red shift-

ed by *ca.* 80 nm from a similar polymer containing benzotropone.^{3e} The conjugated polymer bearing benzotropone showed a quasi-reversible protonation-deprotonation cycle as evidenced by the UV spectroscopy that was supposed to be the character of the carbonyl group of benzotropone.^{3c} To this end, we directed our attention to the synthesis of conjugated polymers bearing tropolone in the main chain. Tropone is predicted to have a nonplanar bent structure and the orbital interaction between p-orbital is considered to be less effective.⁴ On the other hand, some tropolone derivatives demonstrate [1,9]-sigmatropy rearrangement to have a large dipole moment and have a rigid planar structure useful as the mesogenic core in the liquid crystalline materials.⁵ Accordingly, the optical properties of conjugated polymer bearing tropolone are believed to be quite different from those bearing (benzo)tropolone. Tropolone with a free hydroxyl group could form an intramolecular hydrogen bond to behave as a bicyclic compound with fused 5 and 7-membered rings similar to azulene.⁶ The conjugated polymers including an intramolecular hydrogen bond in the repeating unit have been prepared, where the hydrogen bond formation enhanced the electron delocalization along the main chain and brought about a red shift of the absorption spectra.⁷ These polymers not only exhibited different absorption spectra but also demonstrated the stimuli responsive properties.^{7d-f} Hence the influence of an intramolecular hydrogen bond within tropolone unit upon the optical properties of conjugated polymer is also of much interest.

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EXPERIMENTAL

Instruments

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 200 FT-NMR spectrometer using tetramethylsilane (^1H NMR, δ 0.00) or CDCl_3 (^{13}C NMR, δ 77.0) as internal reference peaks. Infrared (IR) spectra were recorded on a Nicolet Impact 400D FT-IR spectrophotometer. Melting points were determined on a YANAGIMOTO micro melting point apparatus. Elemental analyses (EA) were performed by a Yanaco CHN Corder MT-3. Gel permeation chromatographic (GPC) analyses were carried out on a Tosoh DP-8020 using tandem TSK Multipore H_{XL} -M columns (THF as an eluent, flow rate = 1.0 mL/min, 40 °C) equipped with a refractive index detector (RI-8010) on the basis of standard polystyrene samples. Ultraviolet (UV) and photoluminescence (PL) spectra were recorded on a Shimadzu UV-1650PC spectrophotometer and a Shimadzu RF-5300PC spectrofluorometer, respectively, using a 1 cm quartz cell or 1 cm $\times$ 5 cm quartz plate. Quantum yields were determined relative to quinine sulfate in 0.1 N H_2SO_4 with a quantum yield of 0.55.

Materials

Cycloheptanone and boron tribromide were purchased from Kishida Chemical Co., Ltd. Sodium methoxide was purchased from Kanto Chemical Co. Tetrakis(triphenylphosphine)palladium(0) [$\text{Pd}(\text{PPh}_3)_4$] was purchased from TCI. Palladium acetate [$\text{Pd}(\text{OAc})_2$] was purchased from Wako Pure Chemical Industries Ltd. Dichlorobis(triphenylphosphine)palladium(II) [$\text{PdCl}_2(\text{PPh}_3)_2$] and 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) were purchased from Aldrich Chemical Co. These reagents were used as received. 2,7-Diethenyl-9,9-dihexylfluorene,⁸ 2,7-diethynyl-9,9-dihexylfluorene,⁹ 2,5-didecyloxybenzene-1,4-bis(boronic acid),¹⁰ 2,5-didecylbenzene-1,4-bis(boronic acid)¹¹ were synthesized according to the reported protocols. All solvents were dried following to the standard methods and distilled under nitrogen before use. All reactions were performed under nitrogen unless otherwise stated.

Monomer Synthesis

Synthesis of 2,4,7-tribromotropone (**1**). To a mixture of cycloheptanone (25.0 g, 223 mmol) and acetic acid (50 mL) in a three-necked flask equipped with a reflux condenser and a dropping funnel was slowly added bromine (143 g, 894 mmol) dissolved in acetic acid (75 mL) at 0 °C. The reaction mixture was stirred for 12 h at room temperature and for 25 h at 50 °C. Bromine (143 g, 894 mmol) in acetic acid (50 mL)

was again added at 0 °C and the reaction was further performed for 12 h at room temperature and for 25 h at 80 °C. Acetic acid was distilled off and the remaining product was purified by column chromatography (SiO_2 , CH_2Cl_2). Recrystallization from $\text{CH}_2\text{Cl}_2/n$ -hexane gave **1** as a brown solid in 10.2 g (13.4%). Mp. 185–186 °C. ^1H NMR (200 MHz, CDCl_3) δ (ppm) 8.42 (1H, d, J = 1.70 Hz), 7.89 (1H, d, J = 10.18 Hz), 7.25 (1H, dd, J = 1.70, 10.18 Hz). ^{13}C NMR (50 MHz, CDCl_3) δ (ppm) 173.9, 142.3, 138.0, 137.7, 137.5, 133.5, 127.9. IR (KBr) (cm^{-1}) 3049.4, 1607.0, 1577.6, 1556.1, 1397.2, 1347.2, 1210.6, 1112.7, 1017.5, 948.0, 885.4, 856.7, 749.1, 644.1, 567.5, 561.5, 499.8. Anal. Calcd. for: $\text{C}_7\text{H}_3\text{Br}_3\text{O}$: C, 24.53; H, 0.88. Found: C, 24.75; H, 0.99.

Synthesis of *n*,7-dibromo methyltropone (**2**) (n = 4 and 5). To a suspension of **1** (5.00 g, 14.5 mmol) in methanol (20 mL) in a two-necked flask equipped with a reflux condenser was added sodium methoxide (1.10 g, 21.8 mmol). After the exothermic reaction subsided, the mixture was refluxed for 5 h, poured into aq. NH_4Cl , and extracted with CH_2Cl_2 . An organic phase was dried over MgSO_4 and the solvent was removed under the reduced pressure. The crude product was purified by column chromatography (SiO_2 , CH_2Cl_2) to give **2** (an isomeric mixture of 4,7 and 5,7-dibromo methyltropone) as pale yellow oil in 3.56 g (83.4%). ^1H NMR (200 MHz, CDCl_3) δ (ppm) 7.91 (1H $\times$ 0.62, d, J = 2.31 Hz), 7.83 (1H $\times$ 0.38, d, J = 1.86 Hz), 7.67 (1H $\times$ 0.38, d, J = 8.36 Hz), 7.53–7.39 (1H $\times$ 2 $\times$ 0.62 + 1H $\times$ 0.38), 3.92 (1H $\times$ 0.62, s), 3.91 (1H $\times$ 0.38, s). ^{13}C NMR (50 MHz, CDCl_3) δ (ppm) 165.6, 165.1, 136.8, 135.6, 135.4, 134.1, 133.4, 132.4, 130.6, 130.3, 126.4, 122.6, 120.9, 120.3, 52.6, 52.5. IR (KBr) (cm^{-1}) 2956.9, 1736.6, 1606.7, 1575.4, 1457.5, 1433.9, 1374.9, 1347.4, 1284.5, 1245.2, 1146.9, 1111.6, 1088.0, 1029.0, 966.1, 887.5, 828.5, 769.5, 742.0.

Polymerization Procedure

Fluorene-Based Polymer. To a two-necked flask equipped with a reflux condenser containing **2** (0.24 g, 0.80 mmol) and 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (0.40 g, 0.80 mmol) dissolved in THF (18 mL) were added 2 M aq. K_2CO_3 (3.0 mL) and $\text{Pd}(\text{PPh}_3)_4$ (0.09 g, 0.08 mmol). The mixture was refluxed for 15 h and extracted with CH_2Cl_2 . The solvent was evaporated to give a crude product, which was purified by the precipitation into methanol. After drying for 6 h at 50 °C, poly(9,9-dihexylfluorenylidene-alt-methyltropone) (**HFMTp**) was obtained as a pale yellow powder in 0.30 g (80%). M_n = 10400, PDI = 2.4 ^1H NMR (200 MHz, CDCl_3) δ (ppm) 8.14–7.34 (9H, aromatic protons), 3.66 (3H, OCH_3), 2.05 (4H, $\text{CH}_2\text{C}_5\text{H}_{11}$), 1.08 (12H, $\text{CH}_2\text{C}_3\text{H}_6\text{C}_2\text{H}_5$), 0.76

(10H, $C_4H_8C_2H_5$). IR (KBr) (cm^{-1}) 2956.9, 2925.9, 2854.9, 1732.0, 1732.0, 1600.6, 1457.5, 1433.9, 1374.9, 1284.5, 1237.4, 1135.1, 1095.8, 816.7, 789.2.

To a two-necked flask equipped with a vigreux column containing **2** (0.22 g, 0.75 mmol), 2,7-diethynyl-9,9-dihexylfluorene (0.29 g, 0.75 mmol), and sodium acetate (0.31 g, 2.3 mmol) dissolved in NMP (6 mL) was added $Pd(OAc)_2$ (0.017 g, 0.075 mmol). The mixture was heated at 130 °C for 2 d and poured into methanol. The precipitate was collected and dried to obtain poly(9,9-dihexylfluorenylidenevinylene-alt-methyltropolone) (**HFVMTp**) as a yellow powder in 0.14 g (36%). $M_n = 2800$, PDI = 2.1 1H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.91–6.98 (13H, unsaturated protons), 3.66 (3H, OCH_3), 2.02 (4H, $CH_2C_5H_{11}$), 1.08 (12H, $CH_2C_3H_6C_2H_5$), 0.74 (10H, $C_4H_8C_2H_5$). IR (KBr) (cm^{-1}) 2925.5, 2854.1, 1708.6, 1691.3, 1596.8, 1465.6, 1259.3, 1205.3, 958.5, 821.5.

To a two-necked flask equipped with a vigreux column containing **2** (0.22 g, 0.75 mmol) and 2,7-diethynyl-9,9-dihexylfluorene (0.29 g, 0.75 mmol) dissolved in toluene (14 mL) and triethylamine (5 mL) were added CuI (0.014 g, 0.075 mmol) and $PdCl_2(PPh_3)_2$ (0.05 g, 0.075 mmol). The mixture was stirred at room temperature for 2 h and at 60 °C for 3 h, and poured into methanol. The precipitate was collected and dried to obtain poly(9,9-dihexylfluorenylidene-ethynylene-alt-methyltropolone) (**HFEMTp**) as a yellow powder in 0.33 g (81%). $M_n = 3800$, PDI = 2.1 1H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.69–7.53 (9H, unsaturated protons), 4.02 (3H, OCH_3), 1.98 (4H, $CH_2C_5H_{11}$), 1.07 (12H, $CH_2C_3H_6C_2H_5$), 0.81 (6H, $C_5H_{10}CH_3$), 0.64 (4H, $C_4H_8CH_2CH_3$). IR (KBr) (cm^{-1}) 2950.6, 2925.5, 2854.1, 1733.7, 1718.3, 1592.9, 1461.8, 1432.9, 1284.4, 1261.2, 1243.9, 1095.4, 1074.2, 1025.9, 819.6, 802.2.

Benzene-Based Polymer. Poly(2,5-didecyloxyphenylene-alt-methyltropolone) (**DOPMTp**) and poly(2,5-didecylphenylene-alt-methyltropolone) (**DPMTp**) bearing 2,5-didecyloxy-1,4-phenylene and 2,5-didecyl-1,4-phenylene, respectively, were synthesized similarly by Suzuki coupling polymerization. **DOPMTp**: Yield 94%. $M_n = 8400$, PDI = 2.1 1H NMR (200 MHz, $CDCl_3$) δ (ppm) 8.20–6.92 (5H, unsaturated protons), 3.97–3.87 (4H, $OCH_2C_9H_{19}$), 3.74 (3H, OCH_3), 1.73–1.63 (4H, $OCH_2CH_2C_8H_{17}$), 1.23 (28H, $OC_2H_4C_7H_{14}CH_3$), 0.86 (6H, $OC_9H_{18}CH_3$). IR (KBr) (cm^{-1}) 2921.6, 2853.2, 1725.0, 1603.5, 1467.6, 1433.8, 1375.0, 1260.3, 1204.3, 1089.6, 1019.2, 794.5, 693.3. **DPMTp**: Yield 67%. $M_n = 5900$, PDI = 1.9 1H NMR (200 MHz, $CDCl_3$) δ (ppm) 8.00–7.05 (5H, unsaturated protons), 3.68 (3H, OCH_3), 2.62–2.47 (4H, $CH_2C_9H_{19}$), 1.48 (4H, $CH_2CH_2C_8H_{17}$), 1.21 (28H, $C_2H_4C_7H_{14}CH_3$), 0.85 (6H, $C_9H_{18}CH_3$).

IR (KBr) (cm^{-1}) 2933.3, 2847.1, 1733.7, 1720.2, 1600.6, 1465.4, 1433.9, 1288.5, 1241.3, 1084.0.

Polymer Reaction (Transformation to OH Group)

To a CH_2Cl_2 solution (18 mL) of **HFMTp** (0.20 g, 0.43 mmol) in a two-necked flask equipped with a reflux condenser was added BBr_3 (0.38 g, 1.5 mmol) at 0 °C. After refluxing for 20 h, the reaction mixture was poured into iced water and stirred for 1 h. Extraction with CH_2Cl_2 , washing with brine, drying over $MgSO_4$, and evaporation of the solvent gave a crude product. The precipitation into methanol afforded poly(9,9-dihexylfluorenylidene-alt-tropolone) (**HFTp**) having a free hydroxyl group in 0.04 g (21%) as a THF soluble part. $M_n = 9100$, PDI = 2.4 1H NMR (200 MHz, $CDCl_3$) δ (ppm) 8.05–7.65 (9H, aromatic protons), 2.14 (4H, $CH_2C_3H_6C_2H_5$), 1.11 (12H, $CH_2C_3H_6C_2H_5$), 0.86 (10H, $CH_2C_3H_6C_2H_5$). IR (KBr) (cm^{-1}) 2956.9, 2925.5, 2854.9, 1713.0, 1610.8, 1599.0, 1453.6, 1426.0, 1260.9, 1170.5, 1107.6, 1025.1, 820.6, 789.2. Poly(2,5-didecylphenylene-alt-tropolone) (**DPTp**) was likewise prepared in a quantitative yield. $M_n = 7900$, PDI = 2.9 1H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.73–7.18 (5H, unsaturated protons), 2.97–2.66 (4H, $CH_2C_9H_{19}$), 1.75–1.20 (32H, $CH_2C_8H_{16}CH_3$), 0.86 (6H, $C_9H_{18}CH_3$). IR (KBr) (cm^{-1}) 3450.0, 2936.0, 2925.5, 2847.1, 1791.7, 1704.8, 1602.6, 1453.6, 1264.9, 1186.2, 1103.7, 804.9.

RESULTS AND DISCUSSION

Polymerization and Characterization

A tropolone derivative **2** was synthesized by the reaction of **1** with sodium methoxide in methanol under the refluxed temperature. The nucleophilic reaction occurred both at 2 and 7-position to give an isomeric mixture of 4,7 and 5,7-dibromo methyltropolone, where the molar ratio was determined to be 43:57 from the integral ratio of the 1H NMR spectrum. They were directly subjected to the polymerization because the single isomer could not be isolated. Three fluorene-based conjugated polymers with a protected hydroxyl group (**HFMTp**, **HFVMTp**, and **HFEMTp**) were synthesized by the typical Suzuki coupling, Mizoroguchi-Heck, and Sonogashira coupling reactions (Scheme 1). Polymers were obtained as a pale yellow or a yellow powder in good yields. **HFMTp** showed a good solubility in organic solvents to have the highest number-averaged molecular weight ($M_n = 10400$) calculated from the GPC analysis, which corresponded to repeating unit of 22. **HFVMTp** and **HFEMTp** were less soluble and the molecular weights were smaller than **HFMTp**. The polymer structure was confirmed by the 1H NMR spectra. A characteristic

Scheme 1.

signal of tropolone in **HFMTp** was observed at 8.14 ppm, which shifted to downfield region as compared with **2** (Figure 1a). Although the chemical reactivity of two isomers of **2** was expected to be different, the ratio of two repeating unit in these polymers could not be determined. In the IR spectrum of **HFVMTp**, the signal assignable to the C-H out-of-plane bending mode was found at 958 cm^{-1} to indicate that the polymer mainly consisted of *trans* vinylene structure. The C=O stretching vibration signals were observed at 1730 cm^{-1} , 1710 cm^{-1} , and 1734 cm^{-1} for **HFMTp**, **HFVMTp**, and **HFEMTp**, respectively. Those signals shifted to the lower frequency region as compared with monomer **2** (1740 cm^{-1}), which agreed with our previous reports about conjugated polymers having (benzo)tropolone in the main chain.^{3c,3e}

The conversion from the methoxy group to the hydroxyl group was carried out by using BBr_3 (Scheme 2). **HFVTp** and **HFETp** became insoluble in organic solvents probably due to the rigid main chain forced by the intramolecular hydrogen bond within the tropolone unit. From the IR spectrum of **HFVTp**, for example, the O-H vibration signal was observed at 3437 cm^{-1} and the C=O vibration signal (1704 cm^{-1}) shifted to the lower frequency region as compared with **HFVMTp**. This result supported the formation of an intramolecular hydrogen bond. On the other hand, **HFTp** mostly dissolved in THF, CHCl_3 ,

and toluene to have the number-averaged molecular weight of 9100. In the ^1H NMR spectrum, the proton signal of methoxy group at 3.66 ppm completely disappeared and that of tropolone at 8.14 ppm shifted to upfield region to be observed at 7.99 ppm (Figure 1b). The shift of the C=O vibration signal from 1730 cm^{-1} to 1714 cm^{-1} in the IR spectra indicated the formation of an intramolecular hydrogen bond.

DOPMTp and **DPMTp** having the 1,4-phenylene segment were likewise obtained by Suzuki coupling polymerization catalyzed by $\text{Pd}(\text{PPh}_3)_4$ as pale yellow powders in good yields and they had a better solubility than **HFMTp** (Scheme 3). The number-averaged molecular weights of **DOPMTp** and **DPMTp** were estimated by GPC to be 8400 and 5900, respectively. In the ^1H NMR spectrum of **DOPMTp**, the signal of methylene proton adjacent to the oxygen atom split into two parts at 3.97 ppm and 3.95 ppm that reflected the two kinds of repeating unit. The similar trend was observed for the spectrum of **DPMTp**, where the methylene proton signal adjacent to the phenyl ring was detected at 2.62 ppm and 2.47 ppm (Figure 2a). The C=O stretching vibration signals were observed at 1725 cm^{-1} and 1734 cm^{-1} for **DOPMTp** and **DPMTp**, respectively.

The conversion from the methoxy group of **DOPMTp** to the hydroxyl group was conducted by

Figure 1. ^1H NMR spectra of (a) **HFMTp** and (b) **HFTp** in CDCl_3 (200 MHz).

HFTp ($X = \text{nil}$), **HFVtp** ($X = \text{vinylene}$), and **HFETp** ($X = \text{ethynylene}$)

Scheme 2.

Scheme 3.

LiI according to the previous report.¹² Unfortunately, the insoluble product was obtained and the C-O-C vibration signal at 1260 cm⁻¹ obviously decreased in the IR spectrum. We consider that the decyloxy chain was removed from the polymer backbone, probably due to the increased nucleophilicity of iodide anion caused by the coordination of lithium cation to tropolone. The close distance between the decyloxy chain and tropolone might be another important factor. In contrast, soluble **DPTp** could be obtained by using BBr₃ (Scheme 4). The methoxy proton signal at 3.68 ppm completely disappeared in the ¹H NMR spectrum (Figure 2b) and the C=O stretching vibration shifted to the lower frequency region from **DPMTp** (1734 cm⁻¹) to **DPTp** (1707 cm⁻¹). This result supported the formation of a five-membered intramolecular hydrogen bond within the tropolone unit.

Optical Properties

The UV and PL spectra of methyltropolone-containing fluorene-based conjugated polymers (**HFMTp**, **HFVMTp**, and **HFEMTp**) were measured in a CHCl₃ solution (10⁻⁶ M). The absorption maximum wavelength red shifted in the order of **HFMTp** (352 nm) < **HFEMTp** (387 nm) < **HFVMTp** (395 nm) (Figure 3), which followed the normal trend observed in other conjugated polymers. The absorption maximum of **HFMTp** blue shifted by 36 nm as compared with poly(9,9-dihexyl-2,7-fluorene) (388 nm). The emission maximum wavelength also red shifted in the same order. The fluorescence quantum yield

was highest for **HFMTp** (0.68) and dropped to 0.28 of **HFEMTp** based on quinine sulfate as a standard (0.55). In the optical spectra of methyltropolone-containing benzene-based conjugated polymers in a CHCl₃ solution (10⁻⁶ M), **DOPMTp** had longer absorption (350 nm) and emission (447 nm) maximum wavelengths than those of **DPMTp** (269 nm and 385 nm, respectively) (Figure 4), which stemmed from the intramolecular charge transfer between electron donor (decyloxybenzene) and electron acceptor (tropolone). The lower C=O stretching vibration signal of **DOPMTp** (1725 cm⁻¹) than **DPMTp** (1734 cm⁻¹) also supported the presence of the intramolecular charge transfer. The fluorescence quantum yields (0.01 for **DOPMTp** and 0.05 for **DPMTp**) were lower than those of fluorene-based conjugated polymers, which agreed with the large Stokes shift as much as 116 nm and 95 nm for **DOPMTp** and **DPMTp**, respectively.

Finally, the influence of a free-hydroxyl group upon the optical properties of conjugated polymers was investigated with **HFTp** and **DPTp** having the enough solubility to obtain the optical spectra. When the methoxy group was converted to the hydroxyl group, the UV absorption spectra shifted to the longer wavelength region. Namely, the absorption maximum wavelengths of **HFTp** and **DPTp** were observed at 390 nm and 302 nm, respectively (Figure 5). The cut-off wavelength was observed at considerably longer region (550 nm for **HFTp** and 515 nm for **DPTp**). These bathochromic shifts might be ascribed

Figure 2. ^1H NMR spectra of (a) **DPMTp** and (b) **DPTp** in CDCl_3 (200 MHz).

Scheme 4.

to the formation of an intramolecular hydrogen bond between the hydroxyl group and the carbonyl oxygen, which forces the polymer chain more planar to elongate the effective conjugation length. The fluores-

cence emissions were almost quenched in both polymers probably due to the non-radiative decay as observed in the protonation experiment of the benzo-tropolone-containing conjugated polymer.^{3c}

Figure 3. UV and PL spectra of methyltropolone-containing fluorene-based conjugated polymers in CHCl_3 . Closed circle: **HFMTp** (UV), Open circle: **HFMTp** (PL), Closed square: **HFVMTp** (UV), Open square: **HFVMTp** (PL), Closed triangle: **HFEMTp** (UV), and Open triangle: **HFEMTp** (PL).

Figure 4. UV and PL spectra of methyltropolone-containing benzene-based conjugated polymers in CHCl_3 . Closed circle: **DPMTp** (UV), Open circle: **DPMTp** (PL), Closed square: **DOPMTp** (UV), and Open square: **DOPMTp** (PL).

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Figure 5. UV and PL spectra of (a) tropolone-containing fluorene-based conjugated polymers (Closed circle: **HFMTp** (UV), Open circle: **HFMTp** (PL), and Closed square: **HFTp** (UV)) and (b) tropolone-containing benzene-based conjugated polymers (Closed circle: **DPMTp** (UV), Open circle: **DPMTp** (PL), and Closed square: **DPTp** (UV)) in CHCl_3 .

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