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Synthesis of a Novel Optically Tunable Amphiphilic Poly(*p*-phenylene): Influence of Hydrogen Bonding and Metal Complexation on Optical Properties[1]

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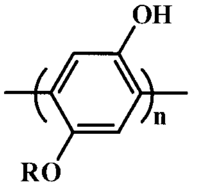
ABSTRACT: A series of optically tunable amphiphilic conjugated polymers, poly(2-hydroxy-5-alkoxy-*p*-phenylene) (**1**) containing long alkyl chains, were prepared by Suzuki polycondensation using 2,5-dibromo-1-benzyloxy-4-alkoxybenzene and bis(boronic ester) monomers. All polymers showed good solubility in common organic solvents such as tetrahydrofuran (THF), chloroform, toluene, and dimethylformamide (DMF). Optical properties of all polymers were investigated in THF at room temperature under neutral conditions, and emission maxima were observed in the violet region ($\lambda_{emi} = 401-403$ nm). By the addition of stoichiometric amount of a base (e.g., aqueous NaOH solution), absorption maxima shifted to the blue region ($\lambda_{emi} = 474-468$ nm). The ionochromic effect of target polymers with transition metal ions such as Fe^{3+}, Cu^{2+}, and Co^{2+} was also reported. In the presence of metal ions, the optical properties of polymers showed interesting tunability of emission maxima, $\Delta\lambda_{max}$ (140−26 nm). X-ray diffraction studies using powdered polymer samples indicated an ordered lamella-type lattice.

Introduction

During the past 2 decades, design and synthesis of conjugated polymers attracted attention due to their interesting optical, electrochemical, and electrical properties, which led to the fabrication of optoelectronic and electronic devices,[2−5] photovoltaic cells,[6] biosensors,[7] to name a few. Synthesis and characterization of a large number of multifunctional conjugated polymers such as poly(*p*-phenylene)s (PPPs),[8−10] poly(*p*-phenylenevinylene)s (PPVs),[11,12] poly(2,5-pyridine)s (PPys),[13,14] polythiophenes,[15,16] polyfluorenes,[17,18] and polyacetylenes[19] have been reported in the literature. Among these polymers, PPP and its derivatives have found considerable interest over the past 20 years due to their high photoluminescence efficiency in blue light-emitting diodes.[20] To enhance the solubility and processability of PPPs, various substituents were introduced along the conjugated polymer backbone, in particular the pioneering synthetic efforts by Wegner et al.[21−24] Owing to the steric interaction between ortho-H atoms of consecutive aryl rings, the extent of π-conjugation was relatively low for these polymers.[25,26] There have been numerous research efforts in planarizing the polymer backbone through covalent bond modification[27−29] or incorporation of weak interactions such as hydrogen bonds.[30,31]

We have designed and synthesized multifunctional poly(*p*-phenylene)s with many free hydroxyl groups on the polymer backbone and explored the possibility of fine-tuning the optical properties by changing environmental conditions such as pH or presence of metal ions. A general structure of our target polymers **1a**−**c** is shown in Scheme 1. In our design strategy, we explored the use of the hydroxyl groups incorporated on the polymer backbone as a hydrogen-bonding functionality to planarize the backbone as well as potential ligand sites for complexation with metal ions. In this paper, we report on synthesis and characterization of three novel polymers and discuss the optical properties in detail.

Scheme 1. Molecular Structure of Target Polymers



1a, R = $CH_3(CH_2)_{11}$−

1b, R = $CH_3(CH_2)_{15}$−

1c, R = $CH_3(CH_2)_{17}$−

Experimental Section

Materials. All reagents were purchased from Aldrich, Fluka, or Merck and were used without further purification unless otherwise stated. All reactions were carried out with dry, freshly distilled solvents under anhydrous conditions or in an inert atmosphere. Tetrahydrofuran (THF) was distilled from sodium benzophenone under a nitrogen atmosphere. Toluene and hexanes were purchased from J.T. Baker and used without further purification.

Measurements. ^1H and ^{13}C NMR spectra were recorded using Bruker AC 300 instruments at 300 MHz for ^1H and 75.47 MHz for ^{13}C, respectively. Thermogravimetric analyses (TGA) were done using TA Instruments SDT 2960 with a heating rate of 10 K/min under a nitrogen atmosphere. Gel permeation chromatography (GPC) was used to obtain the molecular weight of polymers with reference to polystyrene standards using THF as eluent. Absorption and emission spectra of polymers were obtained using a Hewlett-Packard diode array spectrometer and a Perkin-Elmer LS 50B luminescence spectrometer, respectively. IR spectra were recorded using a BIO-RAD FT-IR spectrophotometer. MS spectra were obtained using a Finnigan TSQ 7000 spectrometer with ESI ionization

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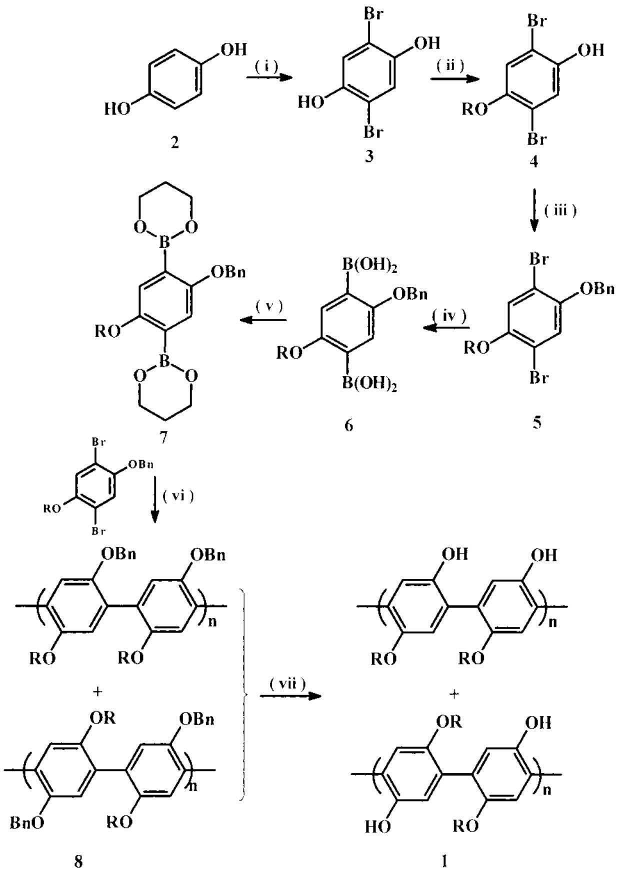
Scheme 2. A General Synthetic Scheme for Polymer 1[a]



[a] (i) Br_2 in gl AcOH, 85%; (ii) NaOH in abs EtOH, RBr, 60 °C for 10 h, 60%; (iii) anhydrous K_2CO_3 in abs EtOH, BnBr, 40−50 °C for 10 h, 95%; (iv) BuLi in hexanes (1.6 M soln), THF/Et_2O at −78 °C, B(O*i*Pr)$_3$, water stirred at RT for 10 h, 80%; (v) 1,3-propanediol, toluene, reflux, 3 h, 80%. (vi) 2 M Na_2CO_3 solution, toluene, 1−1.5 mol % Pd(PPh$_3$)$_4$, reflux for 3 days, (vii) H_2, 10% Pd/C, EtOH/THF. During this study, no attempts were made to establish the regioregularity of the polymers.

capabilities. Elemental analyses were performed using a Perkin-Elmer CHNS autoanalyzer. X-ray powder patterns were obtained using a D5005 Siemens X-ray diffractometer with Cu Kα (1.54 Å) radiation (40 kV, 40 mA). Samples were mounted on a sample holder and scanned with a step size of $2\theta = 0.01°$ between $2\theta = 1.5°$ and 35°.

Synthesis. The synthetic scheme for the monomers and the polymers are outlined in Scheme 2. The experimental procedure for compounds containing hexadecyl and octadecyl alkyl groups are same as compounds with dodecyl alkyl chains. 2,5-Dibromohydroquinone was synthesized using the procedure reported in the literature.[32]

2,5-Dibromo-4-dodecyloxyphenol (4a). 2,5-Dibromohydroquinone **3** (40.2 g, 0.15 mol) was dissolved in 1.5 L of sodium hydroxide (9.2 g, 0.23 mol) solution in absolute ethanol at room temperature under a nitrogen atmosphere. The solution was warmed to 60 °C with constant stirring, followed by the dropwise addition of dodecyl bromide (36 mL, 0.15 mol). After 10 h of stirring under nitrogen atmosphere, the reaction mixture was cooled and filtered, and the precipitate was washed with methanol. It was identified as 2,5-dibromo-1,4-dodecyloxybenzene as a side product. The filtrate was concentrated to remove the solvents. Distilled water (2 L) was added to the residue, and the mixture was acidified with concentrated HCl, boiled gently for 1 h, and cooled. The resulting precipitate was collected by filtration, washed with water, and dried under high vacuum. The crude product was purified by column chromatography on silica gel using a solvent mixture (CH_2Cl_2:hexanes, 4:6) to get the pure product in 60% yield.

(**4a**) ^{1}H NMR ($CDCl_3$, δ ppm): 7.25 (s, 1H,), 6.97 (s, 1H), 5.16 (s, 1H), 3.92 (t, $J = 6$ Hz, 2H), 1.62 (q, 2H), 1.4 (m, 18H); 0.88 (t, $J = 6$ Hz, 3H). ^{1}H NMR ($CDCl_3$ and D_2O, δ ppm): 7.25 (s, 1H,), 6.97 (s, 1H), 3.92 (t, $J = 6$ Hz, 2H), 1.80 (q, 2H), 1.4 (m, 18H); 0.87 (t, $J = 6$ Hz, 3H). ^{13}C NMR ($CDCl_3$, δ ppm): 149.95, 146.64, 120.16, 116.49, 112.34, 108.26, 70.25, 31.81, 29.55, 29.47, 29.26, 29.20, 28.97, 25.82, 22.60, 14.04. Elemental analysis calcd. for $C_{18}H_{28}Br_2O_2$: C, 49.56; H, 6.47; Found: C, 49.17; H, 6.59. FT-IR (KBr, cm^{-1}): 3241, 2911, 2853, 2384, 2337, 1498, 1434, 1386, 1211, 1062, 855, 792, 718. MS (ESI): *m*/*z*: 438, 437, 435, 433.

(**4b**) ^{1}H NMR ($CDCl_3$, δ ppm): 7.24 (s, 1H,), 6.97 (s, 1H), 5.14 (s, 1H), 3.92 (t, $J = 6$ Hz, 2H), 1.80 (q, 2H), 1.4 (m, 26H), 0.86 (t, $J = 6$ Hz, 3H). ^{1}H NMR ($CDCl_3$ and D_2O, δ ppm): 7.24 (s, 1H,), 6.97 (s, 1H), 3.92 (t, $J = 6$ Hz, 2H), 1.80 (q, 2H), 1.4 (m, 26H); 0.86 (t, $J = 6$ Hz, 3H). ^{13}C NMR ($CDCl_3$, δ ppm): 149.5, 146.66, 120.16, 116.53, 112.39, 108.26, 70.28, 31.84, 29.61, 25.84, 22.60, 14.04. Elemental analysis calcd for $C_{22}H_{36}Br_2O_2$: C, 53.67; H, 7.37. Found: C, 51.93; H, 8.10. FT-IR (KBr, cm^{-1}): 3427, 2911, 2841, 2609, 1641, 1503, 1472, 1430, 1385, 1213, 1060, 860, 794, 717. MS (ESI): *m*/*z*: 494, 493, 491, 489.

(**4c**) ^{1}H NMR ($CDCl_3$, δ ppm): 7.24 (s, 1H,), 6.97 (s, 1H), 5.19 (s, 1H), 3.92 (t, $J = 6$ Hz, 2H), 1.82 (q, 2H), 1.4 (m, 30H); 0.87 (t, $J = 6$ Hz, 3H). ^{1}H NMR ($CDCl_3$ and D_2O, δ ppm): 7.24 (s, 1H,), 6.97 (s, 1H), 3.92 (t, $J = 6$ Hz, 2H), 1.82 (q, 2H), 1.47 (m, 26H); 0.87 (t, $J = 6$ Hz, 3H). ^{13}C NMR ($CDCl_3$, δ ppm): 149.96, 146.66, 120.17, 116.53, 112.37, 108.26, 70.27, 31.84, 29.60, 29.60, 28.98, 25.84, 22.60, 14.04. Elemental analysis calcd for $C_{24}H_{40}Br_2O_2$: C, 55.39; H, 7.75. Found: C, 55.26; H, 7.74. FT-IR (KBr, cm^{-1}): 3225, 2917, 2848, 2359, 1498, 1466, 1434, 1386, 1211, 1062, 855, 722. MS (ESI): *m*/*z*: 522, 521, 519, 517.

2,5-Dibromo-1-benzyloxy-4-dodecyloxybenzene (5a). Benzyl bromide (3.8 mL, 0.031 mol) was added dropwise to a stirred solution of 2,5-dibromo-4-dodecyloxyphenol (**4a,** 6.95 g, 0.015 mol) and anhydrous K_2CO_3 (3.28 g, 0.023 mol) in 700 mL of absolute ethanol at 50 °C. The mixture was stirred for 10 h at 50 °C, cooled to room temperature (RT), and concentrated to remove the solvent. An equal volume of distilled water was added to the residue, and the mixture was stirred for 1 h at 0 °C. The resulting precipitate was collected by filtration, washed with water, recrystallized in methanol, and dried under high vacuum to get the pure product in 95% yield.

(**5a**) ^{1}H NMR ($CDCl_3$, δ ppm): 7.46 (m, 5H), 7.21 (s, 1H), 7.15 (s, 1H), 5.11 (s, 2H), 3.99 (t, $J = 6$ Hz, 2H), 1.85 (q, 2H), 1.32 (m, 18H), 0.95 (t, $J = 6$ Hz, 3H). ^{13}C NMR ($CDCl_3$, δ ppm): 150.51, 149.49, 136.16, 128.50, 128.10, 127.17, 119.32, 118.31, 111.53, 111.01, 71.99, 70.19, 31.83, 29.56, 25.84, 22.60, 14.02. Elemental analysis calcd for $C_{25}H_{34}Br_2O_2$: C, 57.05; H, 6.51. Found: C, 57.17; H, 7.31. FT-IR (KBr, cm^{-1}): 2922, 2848, 2359, 1493, 1466, 1355, 1200, 1073, 1004, 855, 802, 754. MS (ESI): *m*/*z*: 528, 526, 453, 451, 425.

(**5b**) ^{1}H NMR ($CDCl_3$, δ ppm): 7.45 (m, 5H), 7.16 (s, 1H), 7.10 (s, 1H), 5.06 (s, 2H), 3.95 (t, $J = 6$ Hz, 2H), 1.80 (q, 2H), 1.26 (m, 26H), 0.88 (t, $J = 6$ Hz, 3H). ^{13}C NMR ($CDCl_3$, δ ppm): 150.43, 149.41, 136.13, 128.49, 127.15, 119.32, 118.31, 111.52, 110.00, 71.98, 70.19, 36.39, 31.81, 29.58, 29.19, 25.82, 22.59, 14.01. FT-IR (KBr, cm^{-1}): 2917, 2848, 1500, 1365, 1216, 1062, 1014, 850, 738. MS (ESI): *m*/*z*: 584, 582, 573, 571, 563, 473, 441, 417, 405.

(**5c**) ^{1}H NMR ($CDCl_3$, δ ppm): 7.37 (m, 5H), 7.14 (s, 1H), 7.09 (s, 1H), 5.05 (s, 2H), 3.93 (t, $J = 6$ Hz, 2H), 1.79 (q, 2H), 1.46 (m, 30H), 0.88 (t, $J = 6$ Hz, 3H). ^{13}C NMR ($CDCl_3$, δ ppm): 150.48, 149.46, 136.13, 128.47, 127.15, 119.30, 118.29, 111.52, 110.00, 71.98, 70.17, 31.81, 28.98, 25.82, 22.59, 14.00. Elemental analysis calcd for $C_{31}H_{46}Br_2O_2$: C, 60.99; H, 7.59. Found: C, 60.63; H, 7.20. FT-IR (KBr, cm^{-1}): 2911, 2848, 2359, 1503, 1466, 1365, 1264, 1222, 1057, 1025, 844, 733. MS (ESI): *m*/*z*: 612, 610, 599, 571, 283.

1-Benzyloxy-4-dodecyloxyphenyl-2,5-bis(boronic acid) (6a). A 1.6 M solution of butyllithium in hexanes (55 mL, 0.088

mol) was added slowly to a solution of dibromide **5a** (11.57 g, 0.022 mol) in an equal volume mixture of diethyl ether (150 mL) and THF (150 mL) under a nitrogen atmosphere at −78 °C. The solution was warmed to RT and recooled to −78 °C, followed by the dropwise addition of triisopropylborate (51 mL) during a period of 2 h. After complete addition, the mixture was warmed to RT, stirred overnight, and mixed with 2 L of deionized water. The crystalline precipitate obtained was collected and recrystallized from acetone in 80% yield.

(**6a**) ^{1}H NMR (DMSO-d_6, δ ppm): 7.80 (s, 2H), 7.75 (s, 2H), 7.46 (m, 5H), 7.29 (s, 1H), 7.17 (s, 1H), 5.11 (s, 2H), 3.99 (t, $J = 6$ Hz, 2H), 1.73 (q, 2H), 1.24 (m, 18H), 0.85 (t, $J = 6$ Hz, 3H). ^{13}C NMR (DMSO-d_6, δ ppm): 157.00, 156.22, 137.16, 128.38, 127.77, 127.52, 118.28, 117.70, 70.05, 68.30, 31.2, 28.89, 25.38, 22.00, 13.87. Elemental analysis calcd for $C_{25}H_{38}B_2O_6$: C, 65.84; H, 8.34. Found: C, 66.09; H, 8.37. FT-IR (KBr, cm^{-1}): 3496, 3352, 2917, 2848, 2359, 1493, 1413, 1392, 1296, 1200, 1052, 796, 727. MS (ESI): *m*/*z*: 456, 455, 454, 453, 437.

(**6b**) ^{1}H NMR (DMSO-d_6, δ ppm): 7.81 (s, 2H), 7.76 (s, 2H), 7.46 (m, 5H), 7.29 (s, 1H), 7.16 (s, 1H), 5.10 (s, 2H), 3.99 (t, $J = 6$ Hz, 2H), 1.69 (q, 2H), 1.23 (m, 26H), 0.84 (t, $J = 6$ Hz, 3H). ^{13}C NMR (DMSO-d_6, δ ppm): 157.02, 156.24, 137.15, 128.36, 127.51, 118.31, 117.74, 70.04, 68.31, 31.20, 28.93, 25.36, 21.98, 13.84. Elemental analysis calcd for $C_{29}H_{46}B_2O_6$: C, 68.01; H, 8.99. Found: C, 67.59; H, 8.98. FT-IR (KBr, cm^{-1}): 3492, 3352, 2917, 2848, 2364, 1498, 1429, 1386, 1296, 1195, 1083, 1052, 795, 727. MS (ESI): *m*/*z*: 512, 511, 510, 421.

(**6c**) ^{1}H NMR (DMSO-d_6, δ ppm): 7.82 (s, 2H), 7.76 (s, 2H), 7.47 (m, 5H), 7.29 (s, 1H), 7.17 (s, 1H), 5.11 (s, 2H), 3.99 (t, $J = 6$ Hz, 2H), 1.73 (q, 2H), 1.23 (m, 30H), 0.83 (t, $J = 6$ Hz, 3H). ^{13}C NMR (DMSO-d_6, δ ppm): 157.04, 156.28, 137.15, 128.38, 127.52, 118.34, 117.76, 70.06, 68.33, 31.21, 28.94, 25.38, 22.00, 13.84. Elemental analysis calcd for $C_{31}H_{50}B_2O_6$: C, 68.93%; H, 9.26. Found: C, 68.14; H, 8.75. FT-IR (KBr, cm^{-1}): 3448, 3363, 2917, 2853, 2359, 1498, 1429, 1392, 1296, 1195, 1057, 781, 722. MS (ESI): *m*/*z*: 540, 539, 538, 449.

1-Benzyloxy-4-dodecyloxyphenyl-2,5-bis(trimethylene boronate) (7a). Diboronic acid (**6a**) (8.2 g, 0.018 mol) and trimethylene glycol (5.2 mL, 0.072 mol) were mixed in 150 mL of dry toluene and refluxed for 3 h. The solvent was removed, and the obtained residue was dissolved in $CHCl_3$, dried over anhydrous sodium sulfate, and filtered. The solid collected after removal of the solvent was recrystallized from hexanes. The recrystllized product was used without further purification for polymerization.

(**7a**) ^{1}H NMR ($CDCl_3$, δ ppm): 7.35 (m, 5H), 5.05 (s, 2H), 4.16 (d, 8H), 3.85 (t, $J = 6$ Hz, 3H), 2.02 (m, 4H), 1.57 (m, 2H), 1.27 (m, 18H), 0.88 (t, $J = 6$ Hz, 3H). ^{13}C NMR ($CDCl_3$, δ ppm): 157.73, 156.92, 138.28, 128.06, 127.00, 120.42, 119.79, 71.70, 69.70, 61.91, 31.81, 29.55, 27.22, 25.98, 22.57, 14.01. FT-IR (KBr, cm^{-1}): 3363, 2917, 2848, 2359, 2337, 1498, 1392, 1296, 1190, 1052, 780, 718. MS (ESI): *m*/*z*: 536, 531, 530, 449.

(**7b**) ^{1}H NMR ($CDCl_3$, δ ppm): 7.35 (m, 5H), 7.21 (s, 1H), 7.14 (s, 1H), 5.04 (s, 2H), 4.17 (d, 8H), 3.84 (t, $J = 6$ Hz, 3H), 1.97 (m, 4H), 1.79 (m, 2H), 1.26 (m, 26H), 0.87 (t, $J = 6$ Hz, 3H). ^{13}C NMR ($CDCl_3$, δ ppm): 157.72, 156.91, 138.06, 128.06, 127.02, 120.43, 119.79, 71.73, 69.70, 61.91, 33.95, 31.81, 29.60, 27.22, 25.97, 22.59, 14.01. FT-IR (KBr, cm^{-1}): 3358, 2911, 2853, 2359, 1493, 1418, 1397, 1296, 1190, 1052, 781, 717. MS (ESI): *m*/*z*: 592, 552, 551, 531, 530.

(**7c**) ^{1}H NMR ($CDCl_3$, δ ppm): 7.34 (m, 5H), 7.21 (s, 1H), 7.14 (s, 1H), 5.04 (s, 2H), 4.14 (d, 8H), 3.85 (t, $J = 6$ Hz, 3H), 2.01 (m, 4H), 1.81 (m, 2H), 1.25 (m, 30H), 0.87 (t, $J = 6$ Hz, 3H). ^{13}C NMR ($CDCl_3$, δ ppm): 157.72, 156.91, 138.27, 128.06, 127.02, 120.42, 119.79, 71.70, 69.62, 62.08, 33.97, 31.81, 29.60, 27.22, 25.98, 22.59, 14.01. FT-IR (KBr, cm^{-1}): 3358, 2911, 2848, 2364, 1503, 1413, 1397, 1291, 1195, 1052, 782, 727. MS (ESI): *m*/*z*: 620, 595, 565, 530.

Poly(1-benzyloxy-4-dodecyloxy-*p*-phenylene) (8a). Diboronic ester **7a** (4.29 g, 8.02 mmol) and dibromo compound **5a** (4.21 g, 8.02 mmol) were mixed in 22 mL of dry toluene under an inert atmosphere. A 70 mL aliquot of Na_2CO_3 solution (2 M) was added to this mixture followed by tetrakis(triphenylphosphino)palladium (1.5 mol % with respect to monomer **5a**) as catalyst. The mixture was stirred at 80 °C for 72 h and precipitated twice from methanol to yield a yellowish polymer, which was filtered and dried in an oven. The obtained yield was 5 g.

(**8a**) ^{1}H NMR ($CDCl_3$, δ ppm): 7.28 (b), 4.97 (b), 3.91 (b), 1.57 (b), 1.27 (b), 0.91 (b). ^{13}C NMR ($CDCl_3$, δ ppm): 150.57, 149.73, 137.79, 128.07, 127.03, 118.06, 116.89, 71.62, 69.41, 31.83, 29.59, 22.59, 14.01. FT-IR (KBr, cm^{-1}): 2916, 2858, 2367, 1413, 1117, 1114, 727, 715.

(**8b**) ^{1}H NMR ($CDCl_3$, δ ppm): 7.26 (b), 4.94 (b), 3.87 (b), 1.5 (b), 1.27(b), 0.89 (b). ^{13}C NMR ($CDCl_3$, δ ppm): 150.72, 149.70, 137.79, 128.07, 127.03, 118.05, 116.86, 71.62, 69.32, 31.83, 29.63, 26.01, 22.59, 14.01. FT-IR (KBr, cm^{-1}): 2922, 2852, 2362, 1453, 1200, 726, 694.

(**8c**) ^{1}H NMR ($CDCl_3$, δ ppm): 7.19 (b), 7.05 (b), 6.9 (b), 4.94 (b), 3.85 (b), 1.5 (b), 1.25(b), 0.87 (b). ^{13}C NMR ($CDCl_3$, δ ppm): 149.70, 148.77, 134.77, 128.17, 127.56, 126.99, 119.35, 71.80, 69.96, 31.83, 29.62, 25.99, 22.59, 14.01. FT-IR (KBr, cm^{-1}): 2911, 2846, 2362, 1469, 1200, 1017, 726, 688.

Poly(1-hydroxy-4-dodecyloxy-*p*-phenylene) (1a). Precursor polymer **8a** (1.32 g) was dissolved in an equal volume mixture of dry THF (50 mL) and absolute ethanol (50 mL) at RT. A 3 g sample of 10% Pd/C and 3 drops of concentrated HCl were added to the solution, and the reaction flask was flushed with nitrogen gas three times to remove traces of oxygen. The debenzylation was carried out at RT under positive pressure of hydrogen for 24 h with constant stirring. The reaction mixture was filtered through Celite powder, and the precipitate was washed with absolute ethanol. The filtrate was evaporated and dried in vacuo to yield the desired polymer (0.8 g).

(**1a**) ^{1}H NMR ($CDCl_3$, δ ppm): 7.04 (b), 6.88 (b), 3.90 (b), 1.77 (b), 1.22 (b), 0.85 (b). FT-IR (KBr, cm^{-1}): 3416, 2922, 2848, 2359, 1647, 1466, 1200, 1025, 802. (**1b**) ^{1}H NMR ($CDCl_3$, δ ppm): 7.04 (b), 6.87 (b), 3.90 (b), 1.77 (b), 1.23 (b), 0.87 (b). FT-IR (KBr, cm^{-1}): 3379, 2914, 2848, 2359, 1615, 1466, 1206, 1052, 807, 722. (**1c**) ^{1}H NMR ($CDCl_3$, δ ppm): 7.03 (b), 6.89 (b), 3.91 (b), 1.75 (b), 1.22 (b), 0.86 (b). FT-IR (KBr, cm^{-1}): 3397, 2916, 2848, 1625, 1469, 1406, 1200, 1054, 796, 720.

Results and Discussion

Synthesis of Polymers. Synthesis of monomers, 2,5-dibromo-1-benzyloxy-4-alkoxybenzene (**5**) and bis(boronic ester) (**7**), and amphiphilic conjugated polymers, poly(2-hydroxy-5-alkoxy-*p*-phenylene) **1a**−**c,** are described in Scheme 2. Bromination of hydroquinone **2** was achieved using a standard procedure.[32] The monoalkylation of dibromo compounds **3** was carried out at 60 °C for 10 h using 1.0 equiv of dibromohydroquinone and 0.9 equiv of alkyl bromide in the presence of a base, sodium hydroxide (1.5 equiv), with ethanol as solvent.[33] The crude product was purified by column chromatography using a 3:2 mixture of hexanes and dichloromethane solvents, and the benzylation of **4** was performed in the presence of anhydrous K_2CO_3 and benzyl bromide to yield compound **5** in 95% yield. Bis(boronic ester) (**7**) was prepared from momomer **5** by reaction with butyllithium and triisopropyl borate,[34] followed by esterification with 1,3-propanediol.[35]

The benzylated precursor polymers were synthesized by Suzuki polycondenzation under standard conditions.[36−38] The polymerization was carried out using equimolar mixture of monomers **5** and **7** in the biphasic medium of toluene and aqueous 2 M sodium carbonate solution with tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] as the catalyst under vigorous stirring for 72 h. The standard workup afforded O-benzylated polymers (**8a**−**c**) as a yellowish precipitate. During this study, no attempts were made to isolate or characterize the regioregularity of the polymers. Hydrogenolysis of precursor polymers **8a**−**c** using palladium adsorbed on

Table 1. Molecular Weights of Target Polymers 1a−c Observed from GPC Analyses[a]

polymer **1**	M_n (g/mol)	M_w (g/mol)	M_w/M_n
1a	3608	4188	1.16
1b	3588	4014	1.11
1c	2634	2851	1.08

[a] The GPC analyses were done at room temperature using fractionated polymers dissolved in THF and filtered; polystyrene standards were used for calibration.

carbon as catalyst gave the target polymers **1a**−**c** in quantitative yield. Polymers **1a**−**c** were further purified using fractional precipitation from methanol.

Characterization of Polymers. All polymers showed good solubility in common organic solvents such as tetrahydrofuran (THF), chloroform, toluene, and dimethylformamide (DMF). Molecular weight of fractionated polymers was determined by gel permeation chromatography (GPC) with reference to polystyrene standards using THF as solvent (Table 1). Most of these fractionated polymers have molecular weights in the range 2−4 kg/mol and polydispersivity index (PDI) around 1.11. However, Müllen et al.[39] reported that GPC results for rigid rod polymers using polystyrene standards were not completely reliable. Similar results were observed for PPPs with polar functional groups on the polymer backbone.[40] For understanding the structure and complexation properties, PPPs with low molecular weight and narrower distribution (PDI close to 1) are preferred.

All neutral polymers were highly stable at room temperature. The thermal properties of all polymers were investigated by thermogravimetric analyses using a heating rate of 10 °C/min under nitrogen. The initial temperature of decomposition of precursor polymers **8a**−**c** ranged from 260 to 294 °C, owing to the decomposition of the benzyl protecting group. For the target polymers **1a**−**c**, the initial decomposition starts from 325 to 350 °C. This may be due to the presence of large alkyl chains along the polymer backbone.

Optical and Ionochromic Properties of Polymers. Optical properties of all polymers were studied using polymer dissolved in doubly distilled THF. The absorption wavelength of benzylated polymers **8a**−**c** showed no significant variation with respect to the length of the side chain from dodecyl (C12) to hexadecyl (C16) groups [$\lambda_{max} = 326$ nm for **8a** and $\lambda_{max} = 326$ nm for **8b**]. The absorption maxima of polymers **1a** and **1b** appeared in the longer wavelength region ($\lambda_{max} = 338$ nm for **1a**, $\lambda_{max} = 336$ nm for **1b)**, presumably due to interchain hydrogen bonding of hydroxyl groups (Figure 1). For polymer **1c**, apparently no changes were observed ($\lambda_{max} = 322$ nm for **8c**, $\lambda_{max} = 322$ nm for **1c)**. It is anticipated that longer alkyl chains, such as the octadecyl (C18) group, were difficult to reorganize as compared to shorter ones, and this could be the reason for this lack of change in absorption maxima. On addition of base such as appropriate amount of aqueous solution of sodium hydroxide ($NaOH_{aq}$), the polymers exhibited a stronger hypsochromic shift to blue region ($\lambda_{max} = 364$ nm for **1a**, $\lambda_{max} = 364$ nm for **1b**, and $\lambda_{max} = 354$ nm for **1c**, all in $NaOH_{aq}$/THF), as shown in Figure 1. This may be due to the formation of phenolate anions on the polymer backbone.[41] The absorbance and emission spectra of neutral polymer (**1a)** with and without an added stoichiometric amount of $NaOH_{aq}$ are shown in Figure 1.

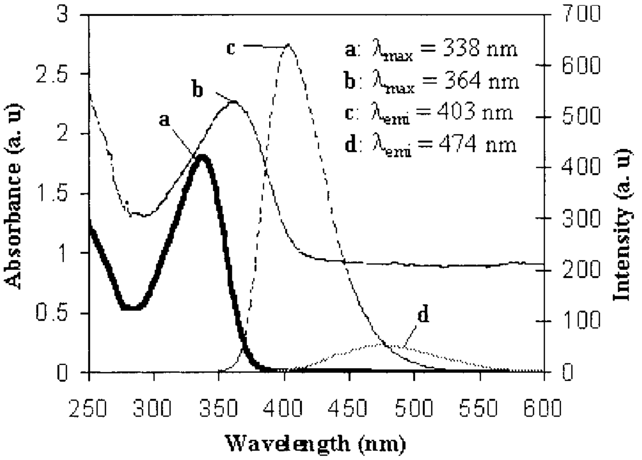


Figure 1. Absorption and emission spectra of polymer **1**: (a) absorption spectrum; (b) absorption spectrum in the presence of a stoichiometric amount of base $NaOH_{aq}$ solution; (c) emission spectrum; (d) emission spectrum in the presence of a stoichiometric amount of base NaOH solution.

The emission spectra of the polymers were recorded using polymers dissolved in freshly distilled THF. The emission maxima of polymers in the presence of a stoichiometric amount of a base such as $NaOH_{aq}$ showed significant differences compared to the neutral polymer as shown in Figure 1. For example, polymer **1a** in THF showed an emission maximum (λ_{emiss}) at 403 nm, but in the presence of $NaOH_{aq}$ the emission maximum of **1a** was shifted to 474 nm. A similar trend was also observed for polymers **1b** and **1c**. All absorption and emission maxima of the target polymers are given in Table 2.

The observed shift in the absorption and emission maxima of polymers **1a**−**c** could be explained using the planarized structure of the polymer backbone (Figure 2). Both hydrogen bonding and alkyl chain crystallization promote the formation of a layer-type morphology for the polymer lattice. This was evident from the X-ray powder diffraction pattern of the polymers. A strong peak at the low angle region corresponding to a *d*-spacing of 34.4 Å (for **1a** with dodecyl group as side chain) indicates a layer-type morphology as shown in Figure 2.

Since each phenyl ring along the polymer backbone carries one alkoxygroup, the observed *d*-spacing value of 34.4 Å implies a noninterdigitated packing of alkyl chains. Similar results were observed for polymers **1a** and **1b**. During this investigation, no attempts were made to isolate possible isomers such as head-to-head or head-to-tail coupling of AA/BB type monomers. In either case, it is expected that the hydroxyl groups and alkyl chains do not mix with each other but get separated to the same side of the polymer backbone. After considering the X-ray diffraction data, an illustration of the expected polymer lattice indicating the possible alkyl chain packing and hydrogen bonding or metal complexation is given in Figure 3.

The ionochromic effect of polymers **1a**−**c** was characterized by the addition of metal salts to the polymer solutions. Color of the polymer solution in THF changed from originally light yellow (metal free polymers) to green, blue or reddish brown, dependent on the type of metal ions added (Table 2). According to the spectroscopic results on metal complexes of the polymers, both **1·Cu**$^{2+}$ and **1·Co**$^{2+}$ complexes emitted in the blue region

Table 2. Absorption and Emission Spectra of Polymers 1a–c with and without Metal Ions[a]

	polymer **1a**		polymer **1b**		polymer **1c**	
	λ_{max} (nm)/E (eV)	λ_{emi} (nm)/E (eV)	λ_{max} (nm)/E (eV)	λ_{emi} (nm)/E (eV)	λ_{max} (nm)/E (eV)	λ_{emi} (nm)/E (eV)
ion-free	338/3.67	403/3.07	336/3.69	402/3.08	328/3.78	402/3.08
Na^+	364/3.40	474/2.61	364/3.40	479/2.59	354/3.50	468/2.65
Cu^{2+}	384/3.23	436/2.84	444/2.79	518/2.39	433/2.86	499/2.44
Co^{2+}	416/2.98	436/2.84	416/2.98	471/2.63	427/2.90	489/2.53
Fe^{3+}	446/2.78	509/2.43	476/2.60	551/2.25	448/2.77	519/2.39

[a] Concentration: polymer **1a**: 0.011 g in 100 mL of THF, polymer **1b**: 0.011 g in 100 mL of THF, polymer **1c**: 0.016 g in 100 mL of THF, Base: stoichiometric amount of base from 1 M aqueous solution of NaOH, 0.1 mL of 1 M metal ion (Cu^{2+}, Co^{2+}, Fe^{3+}) solution in methanol added to the polymer. [Under neutral conditions, benzylated polymers showed absorption maxima (λ_{max}) at **8a** = 326 nm, **8b** = 326 nm; **8c** = 322 nm and emission maxima (λ_{emi}) at **8a** = 400 nm, **8b** = 399 nm, **8c** = 397.5 nm.]

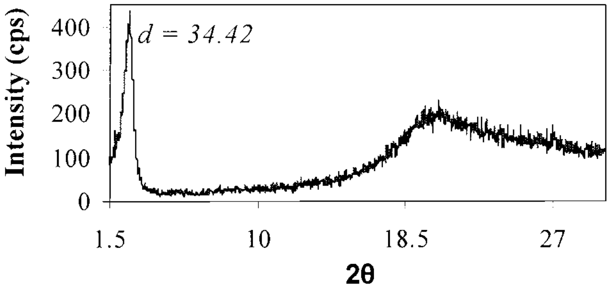


Figure 2. X-ray powder diffraction pattern of polymer **1a**. The powder spectrum was taken using powdered polymer samples placed on the sample pan without preannealing.

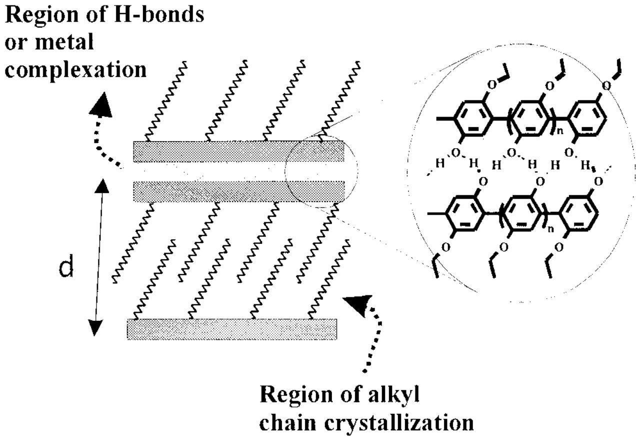


Figure 3. Illustration of the polymer lattice indicating alkyl chain packing and interchain hydrogen bonding.

(λ_{emi} = 464 nm for **1a·Cu**$^{2+}$, 463 nm for **1a·Co**$^{2+}$) and complex **1a·Fe**$^{3+}$ showed a strong emission in the green region (λ_{emi} = 509 nm). Similar results were observed for polymers **1b** and **1c** (Table 2). The absorption wavelengths of previously reported PPP derivatives containing alkyl and alkoxy functional groups were varied from 335 to 280 nm.[6,14,19] It is interesting to note that, by changing the metal ions and thereby the nature of the complex, significant changes in the optical properties of the polymers can be obtained.

To the best of our knowledge, such an ionochromic effect was observed only in conjugated polymers containing bipyridyl units[42,43] and polythiophenes functionalized with oligoethylene oxide side chains.[44] So far, none of the PPP derivatives reported in the literature showed ionochromic effect, and our results indicated that target polymers **1a–c** have strong interaction with metal ions. The absorption and emission maxima of polymers **1a–c** with various metal ions are shown in Table 2, indicating that emission of polymers can be fine-tuned in the blue to green region using a stoichiometric amount of base or metal ions. These results may be of interest to people working in the area of fabricating sensors for metal ions or polymeric light-emitting diodes (PLED) with tunable emission properties.

Conclusions

In conclusion, a novel series of optically tunable amphiphilic conjugated polymers are synthesized using the Suzuki coupling reaction. All polymers showed good solubility in common organic solvents and emission properties in the blue to green region in the presence of base and metal ions. This optical tunability would allow such polymers as good candidates for fabricating PLED devices. The metal chelating effect of these polymers induced significant changes in emission properties and could be used for sensing metal ions. The presence of free hydroxyl groups (phenolic) on the polymer backbone is expected to show interesting electrochemical properties and self-assembly at the liquid–metal interface. We are currently investigating such properties in our laboratory, and the results will be reported at a later date.

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References and Notes

(1) Part of this work was presented at The International Chemical Congress of Pacific Basin Societies, Pacifichem 2000, Honolulu, HI, Dec 2000: Valiyaveettil, S.; Chinnappan, B. Macromolecular Chemistry session, Abs. No. 0072.

(2) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791–804.

(3) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121–128.

(4) McGehee, M. D.; Bergstedt, T.; Zhang, C.; Saab, A. P.; O'Regan, M. B.; Bazan, G. C.; Srdanov, V. I.; Heeger, A. J. *Adv. Mater.* **1999**, *11*, 1349–1354.

(5) Hide, F.; Diaz-Garcia, M. A.; Schwartz, B. J.; Heeger, A. J. *Acc. Chem. Res.* **1997**, *30*, 430–436.

(6) Halls, J. J. M.; Walls, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Nature* **1995**, *376*, 498–500.

(7) Heeger, P. S.; Heeger, A. J. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 12219–12221.

(8) Berresheim, M.; Muller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747–1785.

(9) Yang, Y.; Pei, Q.; Heeger, A. J. *J. Appl. Phys.* **1996**, *79*, 934–939.

(10) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *Macromolecules* **1979**, *12*, 2047–2056.

(11) Scherf, U. *Top. Curr. Chem.* **1999**, *201*, 163–222.

(12) Feast, W. J.; Tsibouklis, J.; Pouwer, K. L.; Groenendaal, L.; Meijer, E. W. *Polymer* **1996**, *37*, 5017–5047.

(13) Blatchford, J. W.; Jessen, S. W.; Lin, L. B.; Gustafson, T. L.; Fu, D. K.; Wang, H. L.; Swager, T. M.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1996**, *54*, 9180–9189.

(14) Yamamoto, T.; Maruyama, T.; Zhou, Z. H.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takeoe, H.; Fukuda, A.; Kubota, K. *J. Am. Chem. Soc.* **1994**, *116*, 4832−4845.
(15) Leclerc, M. *Adv. Mater.* **1999**, *11*, 1491−1498.
(16) Goldenberg, L. M.; Bryce, M. R.; Petty, M. C. *J. Mater. Chem.* **1999**, *9*, 1957−1974.
(17) Setayesh, S.; Marsitzky, D.; Müllen, K. *Macromolecules* **2000**, *33*, 2016−2020.
(18) Uckert, F.; Setayesh, S.; Müllen, K. *Macromolecules* **1999**, *32*, 4519−4524.
(19) Goodson, F. E.; Novak, B. M. *Macromolecules* **1997**, *30*, 6047−6055 and references cited therein.
(20) Cimrova, V.; Schmidt, W.; Rulkiens, R.; Schulze, M.; Meyer, W.; Neher, D. *Adv. Mater.* **1996**, *8*, 585.
(21) Rehan, M.; Schluter, A.-D.; Wegner, G. *Polymer* **1989**, *30*, 1060.
(22) Schülter, A.-D.; Wegner, G. *Acta Polym.* **1993**, *44*, 59.
(23) Vanhee, S.; Rulkens, R.; Lehmann, U.; Rosenauer, C.; Schulze, M.; Kohler, W.; Wegner, G. *Macromolecules* **1996**, *29*, 5136.
(24) Lauter, U.; Meyer, W. H.; Wegner, G. *Macromolecules* **1997**, *30*, 2029.
(25) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350−1377.
(26) Lamba, J. J. S.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11723−11736.
(27) Yao, Y.; Tour, J. M. *Macromolecules* **1999**, *32*, 2455−2461.
(28) Satayesh, S.; Marsitzky, D.; Müllen, K. *Macromoelcules* **2000**, *33*, 2016−2020 and references cited therein.
(29) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghadadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946−953.
(30) Delnoye, D. A. P.; Sijbesma, R. P.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1994**, *118*, 8717−8718.
(31) Pieterse, K.; Vekemans, J. A. J. M.; Kooijman, H.; Spek, A. L.; Meijer, E. W. *Chem. Eur. J.* **2000**, *6*, 4597−4603.
(32) Tietze, L. F. *Reactions and Synthesis in the Organic Chemistry Laboratory*; University Science: Mill Valley, CA, 1989; p 253.
(33) Rehahn, M.; Schluter, A. D.; Wegner, G. *Macromol. Chem.* **1990**, *191*, 1991−2003.
(34) Hensel, V.; Schluter, A. D. *Chem. Eur. J.* **1999**, *5*, 421−429.
(35) Tanigaki, N.; Masuda, H.; Kaeriyama, K. *Polymer* **1997**, *38*, 1221−1226.
(36) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513−515.
(37) Karakaya, B.; Claussen, W.; Gessler, K.; Saenger, W.; Schluter, A. D. *J. Am. Chem. Soc.* **1997**, *119*, 3296−3301.
(38) Yamamoto, T.; Kimura, T.; Schiraishi, K. *Macromolecules* **1999**, *32*, 8886−8896.
(39) Kreyenschmidt, M.; Uckert, F.; Müllen, K. *Macromoelcules* **1995**, *28*, 4577.
(40) Wright, M. E.; Toplikar, E. G.; Lackritz, H.; Subrahmanyan, S. *Macromol. Chem. Phys.* **1995**, *196*, 3563.
(41) Remmers, M.; Schulze, M.; Wegner, G. *Macromol. Chem.* **1996**, *17*, 239−252.
(42) Bouachrine, M.; Lere-Porte, J. P.; Moreau, J. J. E.; Serein-Spirau, F.; Torreilles. *J. Mater. Chem.* **2000**, *10*, 263−268.
(43) Wang, B.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1997**, *119*, 12−21.
(44) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201 and references cited therein.

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