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Control of Conjugation Length and Enhancement of Fluorescence Efficiency of Poly(*p*-phenylenevinylene)s via Post-halogenation

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Post-functionalization of poly(*p*-2,5-dihexyloxy−phenyelenevinylene) (**DHO−PPV**) was studied using *N*-bromosuccinimide (NBS) and *N*-chlorosuccinimide (NCS) in CHCl$_3$ and CHCl$_3$/AcOH to control the color of fluorescence emission and to enhance emission efficiency. It was found that in addition to electrophilic substitution on phenylene rings, halogen and succinimide (in CHCl$_3$) and acetate groups (in CHCl$_3$/AcOH) add across the main chain vinylene groups. With low NXS/PPV reaction ratios (0.1−0.35), where X = Br or Cl, the resulting polymers show poor solubility, a red shift of the absorption maximum, and a decrease in the solid-state fluorescence efficiency (Φ_{fl}), which are explained on the basis of enhanced interchain interactions. For NXS/PPV reaction ratios between 0.5 and 0.75, the solubility of polymers was significantly improved and Φ_{fl} was enhanced by up to 150% due to exciton confinement and a reduction in chain aggregation. For NXS/PPV reaction ratios >0.75, Φ_{fl} decreased dramatically because of an increasing loss of π-conjugation.

Introduction

Poly(*p*-phenylenevinylene)s (PPVs) are the most extensively investigated polymers employed as emitting layers in polymer light-emitting devices (LEDs).[1] They are processable, offer structural diversity, and are highly luminescent. However, as with many conjugated polymers,[1d,e,2] the fluorescence yield is substantially lower in the solid state because of interchain interactions.[3] Strategies to enhance the emission efficiency include the use of copolymers containing wide band gap or insulating segments,[4−7] incorporation of bulky side-chain groups,[8] and the use of polymer blends to isolate the emitting material in a polymer matrix.[3b,9] Another challenge in the development of light-emitting conjugated polymers is tuning of emission wavelength, which is important with respect to full-color displays.[1d,e] The use of segmented conjugated PPVs containing varying conjugation lengths has drawn much attention as a strategy to control the color of emission and to enhance the emission efficiency.[4−7] The enhancement of fluorescence efficiency is considered to be due to trapping and confinement of excitons.[6b,d] One method to obtain segmented conjugated PPVs involves partial elimination

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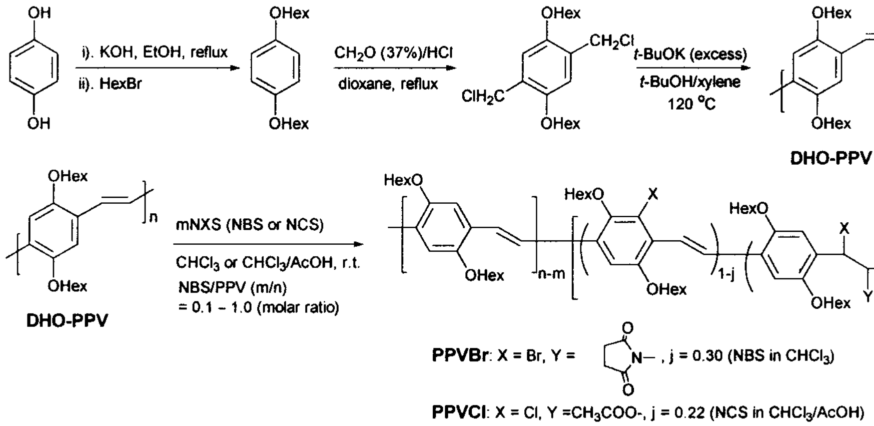
Scheme 1



of nonconjugated precursor polymers through the control of elimination time (or temperature)[6] or the selective elimination of different leaving groups.[7] However, elimination reactions of precursor polymers usually require relatively harsh reaction conditions that lead to difficulty in precise control of conjugation lengths, insolubility of polymers, and the formation of quenching defects.

Recently, we reported a new route to post-functionalize commercially available poly(3-hexylthiophene) via electrophilic substitution and subsequent Pd-catalyzed cross-coupling reactions at the 4-position of thiophene rings.[10,11] Various functional groups, including bromo, chloro, nitro, phenyl, thienyl, furyl, vinyl, and acetylenyl, can be quantitatively anchored to the polymer backbone. It was observed that the absorption maximum of these 3,4-disubstituted poly(thiophene)s exhibited large blue shifts, compared with poly(3-hexylthiophene), because of the twisted polymer backbone. In this work, we apply this strategy to modify a typical PPV derivative, poly(p-2,5-dihexylox-phenyelenevinylene) (**DHO−PPV**), to introduce wide band-gap units into the main chain, and to obtain segmented PPVs. Because **DHO−PPV** possesses an extensively π-conjugated electron-rich backbone, the hydrogen atoms at the 3- and 6-positions of the phenylenes are susceptible to electrophilic substitution. There exists also the possibility to open the vinylene group in the main chain to create nonconjugated segments.[12] By controlling the fraction of nonconjugated units via quantitative post-functionalization, it should be possible to obtain PPVs with desired conjugated lengths to tune the emission color and to enhance the emission efficiency. This paper reports our study on the post-halogenation of **DHO−PPV** using NBS or NCS and describes a simple and mild route to improve processability, to tune the emission color, and to enhance the emission efficiency of PPVs.

Results and Discussion

Synthesis of DHO−PPV. Poly(*p*-2,5-dihexyloxyphenylenevinylene) (**DHO−PPV**) was synthesized by dehydrochlorination of 2,5-bis(chloromethyl)-1,4-dihexyloxybenzene with potassium *tert*-butoxide (Gilch method[15]) in a xylene/*tert*-butyl alcohol mixture solvent as shown in Scheme 1. Aggregation (or gelation) of PPVs often occurs during the Gilch polymerization[16] and approaches to solve this problem have been proposed.[17] In our case, when THF was used as the solvent for polymerization (at room temperature), an insoluble red gel formed. Attempts to prevent gelation by lowering the reaction temperature (0 °C) or addition of 4-*tert*-butylbenzyl chloride[17b,c] were also unsuccessful. When polymerization was carried out in a xylene/*tert*-BuOH (2/1, v/v) mixture solvent, a polymer that is soluble in $CHCl_3$, CH_2Cl_2, THF, and xylene was obtained. However, it was found that the GPC profile of this polymer (dissolved in hot THF and cooled to room temperature for measurement) showed a bimodal molecular weight distribution (Figure 1). Interestingly, when the polymer solution in THF was heated to 50 °C and immediately used for measurement, a monomodal distribution profile was observed. We attribute this phenomenon to strong interchain interactions of **DHO−PPV** at room temperature in THF solution that results in microgelation of polymer chains. The molecular weight and the yield of **DOH−PPV** could be readily controlled by the reaction time with a typical yield of 24−64% and M_n of 28 800−65 100 Da (polystyrene standards). The structure of **DHO−PPV** was confirmed by NMR and FT-IR.

Halogenation of DHO−PPV. When **DHO−PPV** was reacted with an equivalent of NBS (based on the repeating unit) in chloroform at room temperature for

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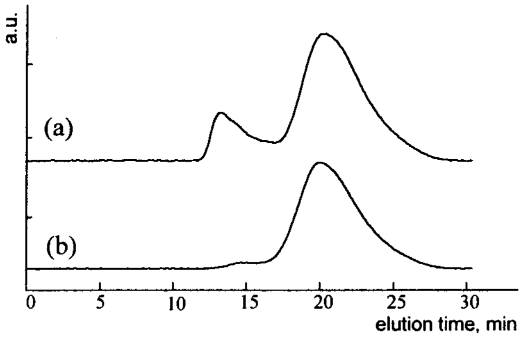


Figure 1. GPC profiles of poly(*p*-2,5-dihexyloxy-phenylenevinylene) (**DHO−PPV**) in (a) cold THF solution (25 °C) and (b) hot THF solution (50 °C).

24 h (Scheme 1), the reaction mixture changed from red to yellow. The ^{1}H NMR spectrum of the reaction mixture indicated that NBS (ethylene protons at 2.92 ppm) was completely converted to succinimide (ethylene protons at 2.78 ppm). ^{1}H NMR spectroscopy of the yellow product (**PPVBr**) showed broad peaks at 7.5 and 7.0 ppm, which are ascribed to unreacted phenylene and vinylene protons (7.53 and 7.19 ppm for **DHO−PPV**), respectively. Additional broad peaks were observed at 6.7 and 6.0 ppm, indicating bromination occurred on phenylene and/or vinylene groups. However, it was inconclusive from ^{1}H NMR alone to determine whether bromination occurred at the phenylene group or the vinylene group. FT-IR (Figure 2), however, showed a decrease in intensity of the phenyl and alkenyl C−H stretching bands at 3057 cm^{-1} and the trans vinylene out-of-plane C−H bending band at 966 cm^{-1},[13] suggesting that bromination occurs at both phenylene and vinylene groups. In addition, a new absorption at 1712 cm^{-1} emerged, ascribed to carbonyl groups. Oxidation of the polymer by molecular oxygen was ruled out because (i) oxygen was rigorously excluded from the reaction and (ii) the intensity of this absorption band increased with an increase in the NBS/PPV reaction ratio (not shown). The possibility of trace NBS, or byproduct succinimide, was also excluded as the cause of this IR band because complete removal of these compounds during workup was confirmed by ^{1}H NMR (no resonance at 2.92 or 2.78 ppm originating from ethylene protons of NBS or succinimide was observed). Therefore, we propose a reaction mechanism as shown in Scheme 2 in which the succinimide anion adds to the bromonium intermediate to form an addition product. In fact, a small broad peak at ≈2.70 ppm was observed in the ^{1}H NMR spectrum, which can be ascribed to ethylene protons in the succinimide unit. From ^{1}H NMR integrals, it is estimated that ≈30% of NBS adds to vinylene groups, while the remainder (70%) is involved in the electrophilic substitution of the phenyl rings. The addition across the vinylene group is also substantiated by bromination of **DHO−PPV** using a mixed solvent, $CHCl_3$/AcOH (5/2, v/v). The resultant polymer (**PPVBr1**) gave no absorption at 1712 cm^{-1} in the IR but instead exhibited a peak at 1752 cm^{-1}. This is interpreted to result from the addition of acetate, rather than succinimide anion, to the bromonium intermediate (Scheme 2). This hypothesis was further proven by bromination of **DHO−PPV** using Br_2 in CCl_4. Under these reaction conditions addition of Br_2 across the vinylene double bond is favored (Scheme 2).[12a] The brominated product (**PPVBr2**) showed neither the peak at 1712 cm^{-1} nor the peak at 1752 cm^{-1} (Figure 2).

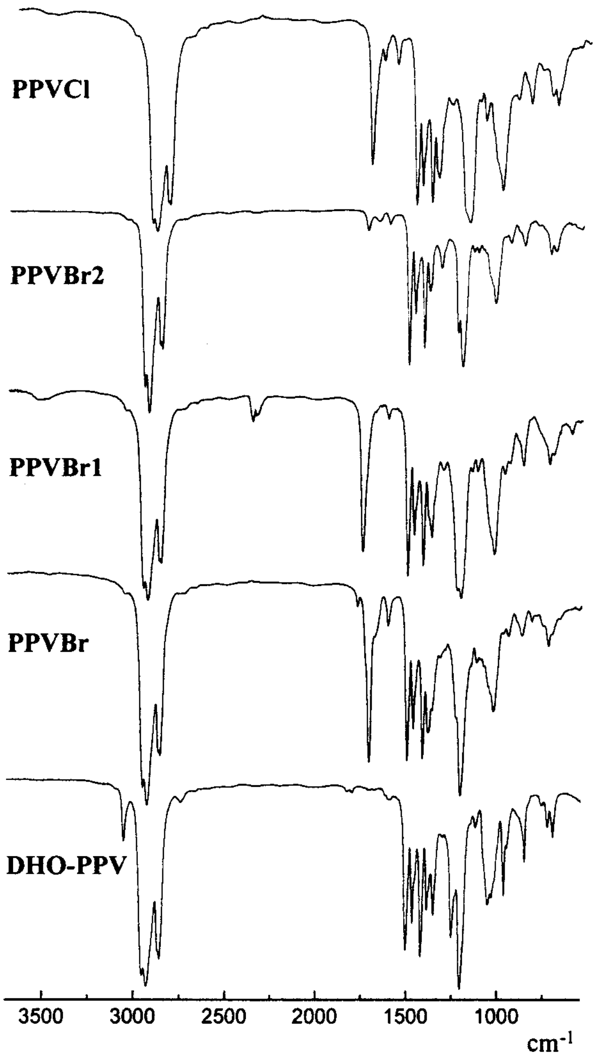
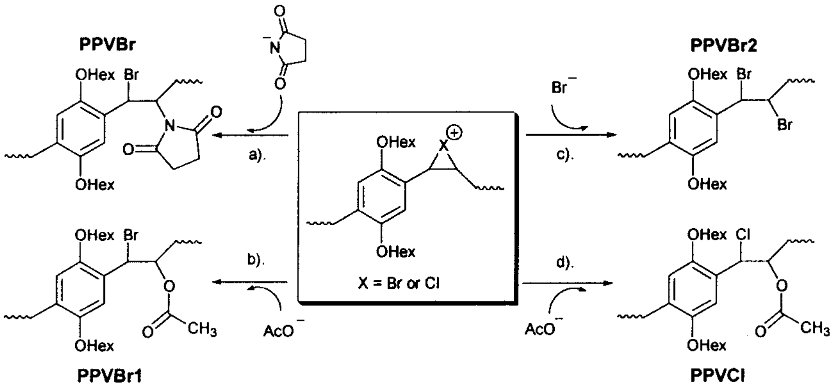


Figure 2. FT-IR spectra of **DHO−PPV**, **PPVBr** (prepared with NBS/PPV = 1 in $CHCl_3$), **PPVBr1** (prepared with NBS/PPV = 1 in $CHCl_3$/AcOH = 5/2, v/v), **PPVBr2** (prepared with Br_2/PPV = 0.5 in CCl_4), and **PPVCl** (prepared with NCS/PPV = 1 in $CHCl_3$/AcOH = 5/2, v/v).

Chlorination of **DHO−PPV** was attempted with an equivalent of NCS in chloroform. After 24 h at room temperature and higher (60 °C), no reaction occurred. When acetic acid (AcOH/$CHCl_3$ = 5/2, v/v) was added to the system, the reaction proceeded. After reaction for 48 h at 60 °C, ^{1}H NMR spectroscopy indicated complete reaction of NCS. ^{1}H NMR and IR (Figure 2) spectra of the chlorinated PPV (**PPVCl**) are similar to those of the brominated PPV (**PPVBr**) prepared in $CHCl_3$/AcOH using NBS, indicating that the addition of chloro and acetate groups to the vinylene group also occurs (Scheme 2). From ^{1}H NMR analysis of the acetate group (2.0−2.2 ppm) it is estimated that ≈22% of NCS reacts across the vinylene groups and 78% predominantly chlorinates the phenylene rings.

Solubility and Aggregation. **PPVBr** and **PPVCl** prepared with NXS/PPV ≥ 0.5 (molar ratio of NXS per repeating unit) showed remarkably improved solubility in common organic solvents, as the result of their more flexible polymer backbone and/or the steric effect of the

Scheme 2



a). NBS, $CHCl_3$; b). NBS, $CHCl_3$/AcOH; c). Br_2, CCl_4; d). NCS, $CHCl_3$/AcOH.

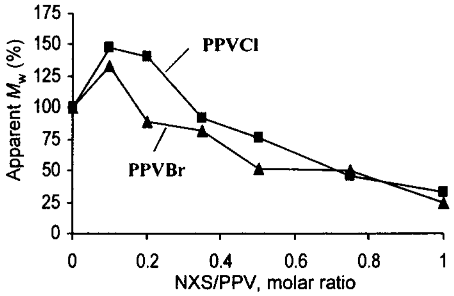


Figure 3. The influence of the NXS/PPV reaction ratio on the molecular weight of polymers (determined by GPC).

Table 1. Solution Photophysical Data for Halogenated PPVs (in THF)

	PPVBr (X = Br)			**PPVCl** (X = Cl)		
	λ_{max} (nm)			λ_{max} (nm)		
NXS/PPV molar ratio	abs.	em.	Φ_{fl}	abs.	em.	Φ_{fl}
0.00	472	546	0.50	472	546	0.50
0.10	474	546	0.51	476	545	0.52
0.20	451	541	0.56	457	543	0.49
0.35	414	529	0.63	422	528	0.62
0.50	395	525	0.66	393	519	0.52
0.75	377	516	0.36	359	493	0.20
1.00	312	465	0.07	309	475	0.03

Table 2. Solid State Photophysical Data for Halogenated PPVs

	PPVBr (X = Br)			**PPVCl** (X = Cl)		
	λ_{max} (nm)			λ_{max} (nm)		
NXS/PPV molar ratio	abs.	em.	Φ_{fl}	abs.	em.	Φ_{fl}
0.00	487	580	0.13	487	580	0.13
0.10	492	581	0.07	493	583	0.07
0.20	464	577	0.10	470	577	0.10
0.35	423	557	0.11	428	580	0.12
0.50	398	545	0.32	396	540	0.20
0.75	380	535	0.27	358	504	0.19
1.00	345	516	0.03	350	479	0.04

incorporated halogen and succinimide (or acetate) groups that prevents chain aggregation. However, when the NXS/PPV reaction ratio was <0.35, the resulting polymers were less soluble than the original **DHO−PPV**. GPC analysis (Figure 3) indicated an abrupt increase in apparent molecular weight with lower NXS/PPV reaction ratios. (Samples were dissolved in hot THF and used for measurement immediately.) The poor solubility and the increase in molecular weight were considered to be due to enhanced intermolecular interactions between polymer chains. It is unclear whether this is caused by the increased polarity of the polymer or a reduction in the polymer's rigidity that facilitates a rapid formation of aggregates. The decrease in apparent molecular weights of polymers for NXS/PPV = 0.35 is ascribed to a further decrease of rigidity of the polymer chain caused by the addition reaction across the vinylene juncture and further losses in π-conjugation along the chain.

Photophysical Properties. The UV−vis absorption and photoluminescence properties of **PPVBr**'s and **PPVCl**'s in solution (Table 1) and in the solid state (Table 2) were investigated. **DHO−PPV** in THF solution displayed an absorption maximum at 472 nm. After halogenation, the resulting polymers were expected to possess shorter conjugation lengths and a blue shift of λ_{max}. However, **PPVBr** and **PPVCl** prepared with NXS/PPV = 0.10 exhibited a λ_{max} at 474 and 476 nm, respectively. The slight red shift with respect to **DHO−PPV** is due to a slight decrease in the optical band gap, caused by the intermolecular aggregation, or the electronic effect of halogen atoms on the phenyl rings. When the NXS/PPV reaction ratio was ≥0.2, the absorption maximum of the halogenated polymers decreased as the NXS/PPV ratio increased, which indicates that conjugation lengths consequently reduce. The emission maximum ($\lambda_{em,\ max}$) of polymers blue shifts gradually from 546 to 465 nm for **PPVBr** and to 475 nm for **PPVCl**, respectively, as the NXS/PPV reaction ratio is increased from 0 to 1. The fluorescence efficiency (Φ_{fl}) of **DHO−PPV** was determined to be 50%. An enhancement of Φ_{fl} (up to 66% for **PPVBr** and 62% for **PPVCl**) was observed when the NXS/PPV reaction ratio increased from 0.10 to 0.5. This can be explained by exciton confinement[6b,d] in the "quantum well" of these segmented conjugated polymers (Figure 4). A further increase in the NBS/PPV reaction ratio (≥0.75) yields polymers with decreasing Φ_{fl}. At these levels of post-functionalization the polymers possess substantially reduced degrees of π-conjugation.Solid-state UV−vis absorption spectra of polymers prepared from NXS/PPV = 0.1 showed a red shift of λ_{max} (Table 2). Polymers prepared from NXS/PPV ≥ 0.2 gave absorption maxima that blue shift with increasing reaction ratios, resulting from dissociation of polymer chains and the shortening of conjugation lengths. Fluorescence data showed that emission maxima ($\lambda_{em,max}$,s) were similar for polymers prepared from NXS/PPV = 0−0.35 (Figure 5). As the

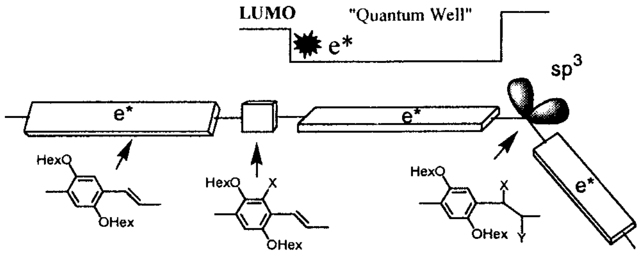


Figure 4. The exciton confinement effect in halogenated **DOH−PPV**.

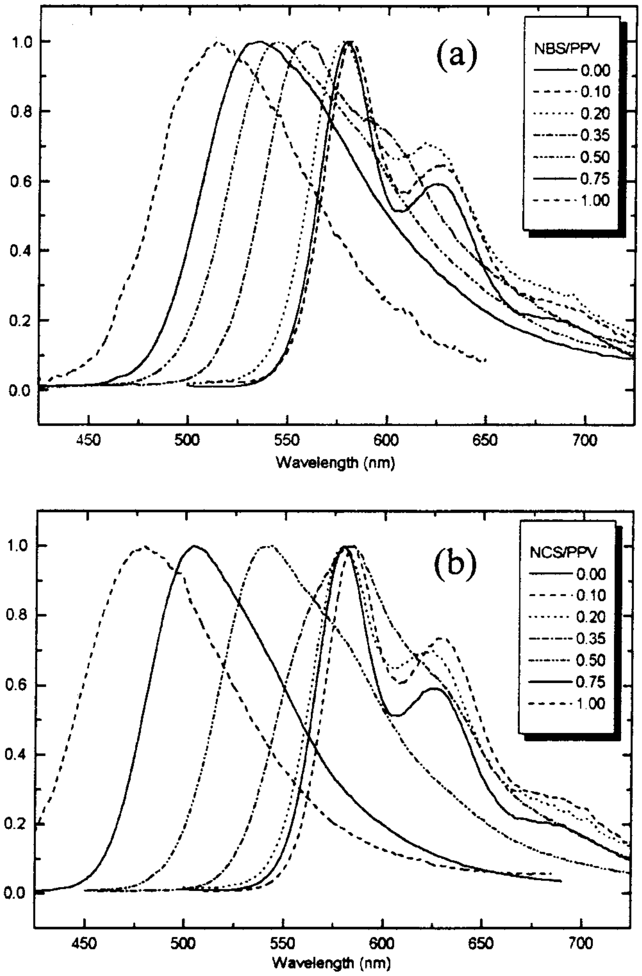


Figure 5. Solid-state fluorescence spectra: (a) **PPVBr** and (b) **PPVCl**.

NXS/PPV reaction ratio increased from 0.35 to 1, the emission maximum blue-shifted from 557 to 516 nm for **PPVBr** and from 580 to 479 nm for **PPVCl**. π-Stacking and/or aggregation of conjugated polymers in the solid state usually causes a red shift in the emission spectrum relative to solution spectra.[18] $\lambda_{em,max}$ of the **DHO−PPV** film red-shifted 34 nm compared to its dilute THF solution and Φ_{fl} decreased dramatically from 50% in solution to 13% in the solid state. With lower NXS/PPV reaction ratios (0.10−0.35), polymer films also showed large red shifts in $\lambda_{em,max}$ relative to the solution phase and Φ_{fl} of these polymers are even lower than that of **DHO−PPV** (Table 2). These results support the assumption of enhanced interchain interactions. When the NXS/PPV reaction ratio was increased to 0.50−0.75, the interchain interactions are suppressed, which is manifested by a smaller red shift of $\lambda_{em,max}$, compared with the solution phase. Φ_{fl} of polymer films increases up to 32% for **PPVBr** and 20% for **PPVCl**. This is believed to be the result of the above-mentioned exciton confinement effect associated with segmentation and the steric effect associated with both the halogenated phenylene and the vinylene groups that inhibit interchain face-to-face quenching. More heavily halogenated polymers (NXS/PPV $\geq$ 1) gave only weak emission, as destruction of the π-conjugated system nears completion.

Conclusion

Post-halogenation of **DHO−PPV** with NBS and NCS under mild conditions modifies the structure and properties of this polymer. Halogenation occurs at both phenylene and vinylene groups; the former produces more sterically encumbered phenylene groups with wide band gaps, while the latter affords saturated units. The solubility of the resulting polymers is decreased when the extent of post-functionalization is limited, but increases with increasing degrees of reaction. These polymers, both in solution and in the solid state, show a red shift in λ_{max} with low degrees of post-fuctionalization but blue shift upon further reaction. Fluorescence efficiency of these polymers in solution increases when the NXS/PPV reaction ratio lies between 0.1 and 0.5 and falls as the NXS/PPV reaction ratio is further increased. Polymers from NXS/PPV = 0.50−0.75 displayed a 150% and 50% enhancement in Φ_{fl} in the solid state for bromo and chloro derivatives, respectively.

The above results indicated that interchain interactions exist in polymers prepared with lower degrees of post-reaction, but with further reaction, aggregation of polymer chains can be suppressed, which leads to the enhancement of Φ_{fl} in the solid state. This study provides a new method to control the emission color and enhance the fluorescence efficiency of PPVs and illustrates the role of aggregation on their photophysical properties.

Experimental Section

Measurements. 400-MHz ^{1}H and 100-MHz ^{13}C NMR spectra were obtained in $CDCl_3$ or CD_2Cl_2 on a 400-MHz Bruker AMX400 spectrometer; the chemical shifts are reported in ppm, referenced to $CHCl_3$ (δ 7.26) or $CDHCl_2$ (δ 5.32) in ^{1}H NMR and to $CDCl_3$ (δ 77.0) in ^{13}C NMR, respectively. IR spectra were recorded on a Bomen Michelson MB series spectrophotometer. UV−vis absorption spectra were obtained on a Cary 3E (Varian) spectrophotometer. Fluorescence measurements were carried out on a PTI QuantumMaster model QM-1 spectrometer. Polymer solutions in THF with o.d. = 0.05−0.1 were deoxygenated prior fluorescence measurement and the quantum yield of polymers was determined against quinine bisulfate standard (Φ_{fl} = 0.546 in 1.0 N H_2SO_4). Spin-coated polymer films with o.d. = 0.1−0.2 were protected under an argon flow during fluorescence measurement and the quantum yield was reported against 9,10-diphenylanthracene in PMMA ($<10^{-3}$ M) (Φ_{fl} = 0.83). Gel permeation chromatography (GPC) analysis of polymers was conducted on a Waters Model 510 HPLC equipped with μ-Styragel columns using THF as an eluent with polystyrene as standards. Elemental analysis was performed by Canadian Microanalytical Service Ltd.

Materials. *N*-Bromosuccinimide (NBS) and *N*-chlorosuccinimide (NCS) were purchased from Aldrich and used as

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[18] Cornil, J.; dos Santos, D. A.; Crispin, X.; Silbey, R.; Brédas, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 1289.

received. Chloroform and carbon tetrachloride were dried over CaH_2 and distilled prior to use. 1,4-Dihexyloxybenzene and 2,5-bis(chloromethyl)-1,4-dihexyloxybenzene were prepared according to reported methods.[13,14]

Synthesis of Poly(*p*-2,5-dihexyloxy−phenylenevinylene) (DHO−PPV) (Gilch Method[15]). To a 1-L flask under nitrogen were charged 2,5-bis(chloromethyl)-1,4-dihexyloxybenzene (6.0 g, 16 mmol), potassium *tert*-butoxide (9.0 g, 80 mmol), xylene (400 mL), and *tert*-butyl alcohol (200 mL). The mixture was heated to and maintained at 120 °C for 12−24 h. The red-orange color solution was then poured into ethanol (2 L). The red precipitate was collected and extracted with refluxing methanol for 24 h and then dissolved with chloroform. The concentrated solution was poured into methanol and a red solid was obtained, which was dried under vacuum for 24 h. Yield: 24−64%. ^{1}H NMR (CD_2Cl_2): δ 7.53 (m, 2H, aromatic), 7.19 (br, 2H, vinylene), 4.08 (br, 4H, $PhOCH_2-$), 1.88 (m, 4H, $PhOCH_2CH_2-$), 1.53 (m, 4H, $PhOC_4H_8CH_2CH_3$), 1.39 (br, 8H, $PhOC_2H_4C_2H_4CH_2CH_3$), 0.93 (br, 6H, $PhOC_5H_{10}CH_3$). ^{13}C NMR ($CDCl_3$): δ 151.10, 127.49, 123.24, 110.51, 69.50, 31.67, 29.52, 28.32, 25.96, 22.66, 14.05. IR (neat): 3057, 2954, 2930, 2859, 1505, 1468, 1421, 1388, 1353, 1253, 1205, 1056, 966, 852, 699 cm^{-1}.

Bromination of DHO−PPV with NBS in $CHCl_3$ (PPVBr). A typical procedure is as follows. To a 20-mL Schlenk flask containing **DHO−PPV** (50.0 mg, 0.165 mmol) in chloroform (5 mL) was added NBS (29.4 mg, 0.165 mmol). The solution was stirred at room temperature in the absence of light for 24 h. The reaction mixture was then poured into a saturated $NaHCO_3$ solution (20 mL). The organic layer was washed with water 5 times and dried over $MgSO_4$. After the solvents were evaporated, the polymer was dissolved in chloroform and passed through a silica gel column. With the solvent evaporated, a yellow solid was obtained (57.6 mg). ^{1}H NMR: δ 7.5 (br), 7.0 (br), 6.7 (br), 6.0 (br), 3.88 (br, $PhOCH_2-$), 2.70 (br), 1.75 (br), 1.52 (br), 1.34 (br), 0.90 (br, CH_3). IR (neat): 2954, 2931, 2859, 1712, 1503, 1469, 1417, 1386, 1208, 1029, 872, 727 cm^{-1}. Elemental analysis: C, 64.98; H, 7.66; Br, 13.72.

Bromination of DHO−PPV with NBS in $CHCl_3$/AcOH (PPVBr1). A similar procedure as described above was employed except a mixed solvent $CHCl_3$/AcOH (5 mL/2 mL) was used in place of chloroform. IR (neat): 2954, 2931, 2859, 1752, 1504, 1469, 1419, 1372, 1209, 1028, 870, 726 cm^{-1}.

Bromination of DHO−PPV with Br_2 in CCl_4 (PPVBr2). To a 20-mL Schlenk flask containing **DHO−PPV** (50.0 mg, 0.165 mmol) in CCl_4 (5 mL) was added bromine (1.06 mL, 0.155 M Br_2 solution in CCl_4) at 0 °C. The solution was stirred at room temperature in the absence of light for 4 h. A similar workup procedure as above gave a yellow solid. IR (neat): 2954, 2930, 2870, 2859, 1504, 1469, 1418, 1390, 1325, 1233, 1207, 1028, 866, 725 cm^{-1}.

Chlorination of DHO−PPV (PPVCl). A typical procedure was given as follows. To a 20-mL Schlenk flask containing **DHO−PPV** (50.0 mg, 0.165 mmol) in $CHCl_3$/AcOH (5/2 mL) was added NCS (22.0 mg, 0.165 mmol). The solution was stirred at 60 °C in the absence of light for 48 h. A similar workup procedure as above gave a yellow solid. ^{1}H NMR: δ 6.5−7.5 (br), 3.86 (br, $PhOCH_2-$), 3.30 (br), 1.75 (br), 1.34 (br), 0.90 (br, CH_3). IR (neat): 2955, 2931, 2860, 1750, 1503, 1469, 1417, 1380, 1208, 1029, 872, 726 cm^{-1}. Elemental analysis: C, 68.24; H, 8.74; Cl, 9.13.

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