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Precise Synthesis of Poly(fluorene-2,7-vinylene)s Containing Oligo(thiophene)s at the Chain Ends: Unique Emission Properties by the End Functionalization

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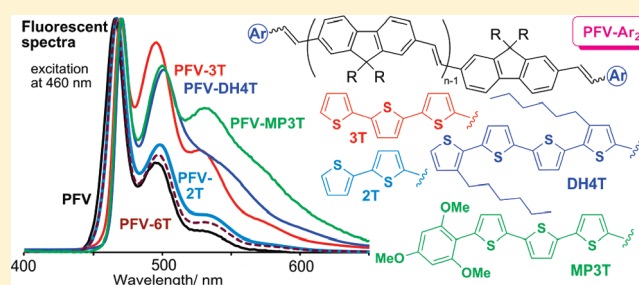
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S Supporting Information

ABSTRACT: Poly(9,9-di-*n*-octylfluorene-2,7-vinylene)s (PFVs) containing an oligo(thiophene) moiety at the chain ends have been prepared and identified. Fluorescence spectra of PFVs containing 3 or 4 thiophene repeat units at the chain ends showed significant difference in their intensities at ca. 500 and 530 nm from those containing others (2 or 5 thiophene repeat units, etc.). The emission intensities were dependent upon the degree of fluorene-2,7-vinylene repeat unit (PFV conjugation length); the observed differences are thus attributed to an energy transfer from the PFV conjugated main chain to the oligo(thiophene) moieties.



INTRODUCTION

Organic electronics are one of the most important emerging technologies, and conjugated polymers, such as poly(*p*-arylenevinylene)s and poly(thiophene)s, are promising semiconducting materials.^{1–6} A subject concerning synthesis of structurally regular, chemically pure polymers by the development of new synthetic methods attracts considerable attention^{1–3} because their device performances are generally affected by polymer structural regularity, chemical purity, and supramolecular order.^{4–6} Fluorene-based electroluminescent (EL) polymers are known to be promising in terms of a facile introduction of substituents into the C₉ position, high photoluminescence (PL) and EL efficiencies, and thermal and chemical stabilities.^{7–10} Synthesis of structurally regular, chemically pure polymers by development of new synthetic methods attracts considerable attention¹ because their device performances are affected by polymer structural regularity, chemical purity, and supramolecular order.^{2–4}

We reported that stereoregular (*all-trans*), high molecular weight poly(9,9-dialkylfluorene-2,7-vinylene)s (PFVs) could be prepared by acyclic diene metathesis (ADMET) polymerization of 9,9-dialkyl-2,7-divinylfluorene using Mo(N-2,6-Me₂C₆H₃)-(CHCMe₂Ph)[OCMe(CF₃)₂]₂ (**Mo**)⁷ or RuCl₂(PCy₃)(IMes-H₂)(CHPh) [**Ru**, Cy = cyclohexyl, IMesH₂ = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene]^{8,9} under optimized conditions.¹¹ The conditions for synthesis of PFVs⁸ were also effective for syntheses of high molecular weight poly(2,5-dialkylphenylene-1,4-vinylene)s (PPVs).¹² The facts introduced interesting contrast because the initial

attempts for synthesis of PPVs by this approach afforded oligomer mixtures.^{13,14}

Although the strict control of the repeating units cannot be attained in the present ADMET condensation polymerization (M_w/M_n = ca. 2), the resultant polymers possessed the following promising characteristics: (1) defect free without termination of conjugated units, any negative impurities (halogen, sulfur, etc.) and (2) highly *trans* olefinic double bonds (because the reaction proceeds via metallacycle intermediate^{13,14}). Moreover, the resultant polymers prepared by **Ru** possessed well-defined polymer chain ends (as vinyl group),^{8,9} and we thus demonstrated more recently that a facile, exclusive end functionalization can be achieved by treating the vinyl groups in PFV with **Mo** followed by Wittig-type cleavage with 4-Me₃SiOC₆H₄CHO; precise synthesis of ABA type amphiphilic triblock copolymers had thus been accomplished by grafting PEG into both the PFV chain ends (Scheme 1).⁸

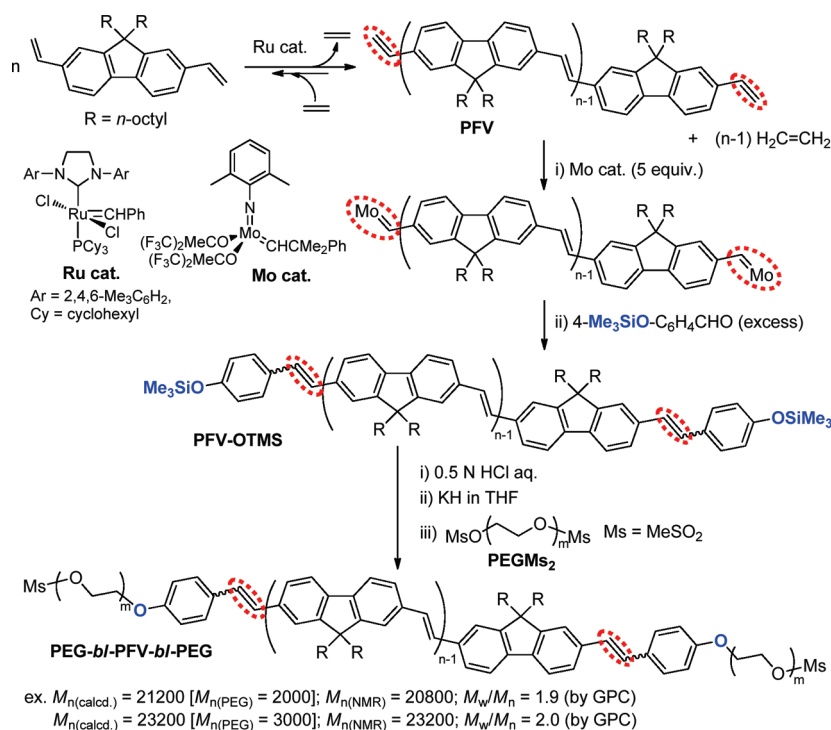
On the basis of the above results, we thus focus on the synthesis of various PFVs containing functionalities at the both polymer chain ends by adopting this approach. It should be stressed that successful examples of precise synthesis of telechelic conjugated polymers (containing functional group at the both chain ends) have been limited,^{15,16} although they paved the way to the formation of regular one-dimensional conjugated structures

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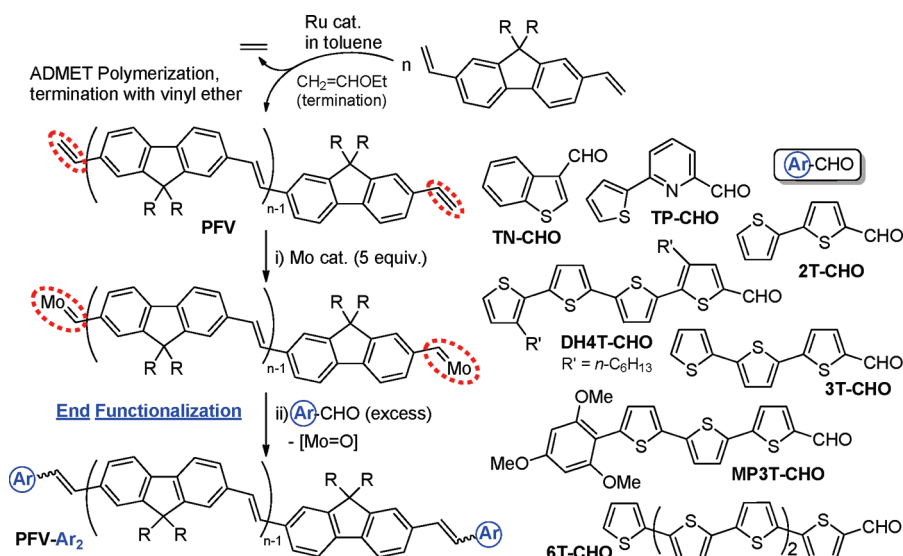
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Scheme 1. Precise Synthesis of Amphiphilic Triblock Copolymers Consisting of Poly(ethylene glycol) (PEG) and Poly(fluorene-2,7-vinylene) (PFV) Prepared by Acyclic Diene Metathesis (ADMET) Polymerization⁸



Scheme 2



on the nanoscale from the assembling properties of rod-coil block copolymers. Through this approach, we herein present the synthesis of PFV's containing oligo(thiophene)s in the both chain ends by adopting the approach, as a demonstration of functionalization of a conjugated polymer at the end groups by π -systems (Scheme 2). We also wish to present that the emission property in the resultant conjugated polymers can be modified by introduction of oligo(thiophene) moieties at the chain ends.^{17,18}

RESULTS AND DISCUSSION

Synthesis of End-Functionalized PFVs. Acyclic diene metathesis (ADMET) polymerization of 2,7-divinyl-9,9-di-*n*-octylfluorene^{8,9} was conducted in the presence of **Ru** catalyst according to the established conditions under a reduced pressure (reaction time 3 h). The resultant poly(9,9-di-*n*-octylfluorene-2,7-vinylene) (PFV) possessed high molecular weight with unimodal molecular weight distribution (by GPC analysis: $M_n = 2.60 \times 10^4$,

$M_w/M_n = 1.96$).¹⁹ Removal of ethylene byproduct from the reaction medium is a prerequisite for obtaining of the high molecular weight polymers in this catalysis,^{7–9} and rather low molecular weight PFV was obtained when the reaction was terminated at short period (1 h, by GPC analysis: $M_n = 1.67 \times 10^4$, $M_w/M_n = 2.19$). As demonstrated previously,^{8,9} the resultant PFVs possessed exclusive *trans* regularity as well as vinyl groups at the both polymer chain ends as confirmed by ¹H NMR spectra.

According to our reported procedures,⁸ the vinyl groups at the PFV chain ends were treated with **Mo** (2.5 equiv to the vinyl group, to generate Mo–alkylidene moieties) and the subsequent addition of excess amount (ca. 2 equiv to **Mo**) of various aldehydes (ArCHO) gave PFVs containing functionalities at the both polymer chain ends (PFV-Ar₂, Scheme 2). The results are summarized in Table 1, and the ¹H NMR spectra are shown in the Supporting Information.²⁰ Slight increases in the M_n values in the resultant polymers after treatment with ArCHO were observed by GPC measurement in most cases, and the results were reproducible (runs 4 and 5): protons corresponding to the chain ends could be observed in the ¹H NMR spectra.²⁰ As reported previously,^{8,9} the M_n value estimated by ¹H NMR spectrum (by integration ratio, run 6, $M_{n(\text{NMR})} = 11\,400$) was close to the exact value estimated from the M_n value by GPC ($M_{n(\text{calc})} = 11\,800$).²¹ The fact thus strongly suggests that, as

Table 1. Precise Synthesis of End-Functionalized Poly(9,9-di-*n*-octylfluorene-2,7-vinylene)s (PFV-Ar₂)^a

run	PFV			PFV-Ar ₂		
	$M_n^b \times 10^{-4}$	M_w/M_n^b	ArCHO ^c	$M_n^b \times 10^{-4}$	M_w/M_n^b	yield ^d /%
1	2.60	1.96	TN-CHO	2.71	1.96	98
2	2.60	1.96	TP-CHO	2.64	1.98	98
3	2.60	1.96	2T-CHO	2.68	1.95	96
4	2.60	1.96	3T-CHO	2.77	1.93	>99
5 ^e	2.60	1.96	3T-CHO	2.64	2.02	>99
6	1.67	2.19	3TCHO	1.72 ^f	2.12	93
7	2.60	1.96	MP3T-CHO	2.81	1.93	93
8	2.60	1.96	DH4T-CHO	2.60	2.01	>99
9	2.60	1.96	6T-CHO	2.75	1.92	>99

^aDetailed conditions are shown in Scheme 2 and the Experimental Section. ^bGPC data in THF vs polystyrene standards. ^cArCHO shown in Scheme 2. ^dIsolated yields. ^eIndependent runs for reproducibility. ^f $M_n = 1.18 \times 10^4$ (estimated by GPC data: $M_{n(\text{GPC})}/1.6 + 3T$) vs $M_n = 1.14 \times 10^4$ (by ¹H NMR based on integral ratio).

shown in Scheme 2, precise, exclusive syntheses of PFVs (PFV-Ar₂) containing substituted thiophenes or (oligo)thiophene moieties at both polymer chain ends have been achieved by adopting the present approach.

UV–vis and Fluorescence Spectra for PFV-Ar₂. Figure 1 shows (a) UV–vis spectra and (b) fluorescence spectra (excitation wavelength at 460 nm) for various PFVs containing (oligo)thiophene moiety at the polymer chain ends (PFV and PFV-Ar₂, 1.0×10^{-6} M in THF at 25 °C). As reported previously,^{7,9} the UV–vis spectrum for PFV (before modification) displays two absorption bands at 427 and 455 nm, which can be attributed to π – π^* transitions of the conjugated backbone, which can be attributed to π – π^* transitions of the conjugated backbone.^{10e} No significant changes were observed in the spectra for PFVs after introduction of functionalities (Ar group, Figure 1a); the spectra for PFV-TP and PFV-TN were also analogous to that for PFV-2T.²⁰

Figure 1b shows fluorescence spectra (in THF, 1.0×10^{-6} M at 25 °C, excitation wavelength at 460 nm) for various PFVs containing (oligo)thiophene moiety at the polymer chain ends (shown in Scheme 2). The spectra in most PFVs with excitation at 460 nm showed a strong emission band at ca. 465 nm with a shoulder at 496 nm along with a slight shoulder at 530 nm (Figure 1b). It is already explained that the shoulder arises from coupling between the fluorene and vinylene units to form a new electronic state with a lower energy.²²

Note that the spectra for PFVs containing three or four thiophene repeat units (PFV-3T, PFV-MP3T, PFV-DH4T) were apparently different from those for PFV and the others (PFV-2T, PFV-6T). In particular, the intensities at ca. 497–500 and 528–531 nm for these polymers (PFV-3T, PFV-MP3T, PFV-DH4T) were higher than those for the others (PFV, PFV-2T, PFV-6T). The spectra for PFV-TN, PFV-TP were also close to that for PFV-2T.²⁰ It thus seems likely that a certain number of thiophene repeat units (3–4) would be important for the unique observation in the fluorescence spectra.

In order to clarify this observation in the fluorescence spectra (by PFV-3T, PFV-MP3T, PFV-DH4T), the spectra for PFV-3T were measured in various solvents (THF, chloroform, toluene at 25 °C, Figure 2a) at various temperatures (in THF at –5 to 50 °C, Figure 2b). This is because that one appropriate assumption for explaining the observed fact may be due to an aggregation of the oligo(thiophene) moieties at the polymer chain ends. However, importantly, no significant changes in the spectra were observed even if the spectra were measured in various solvents at various temperatures; no apparent differences in the spectra were observed for other PFVs (PFV, PFV-2T, PFV-6T) measured at

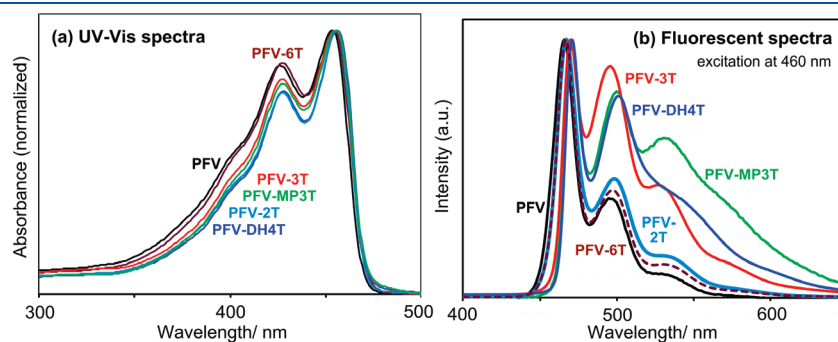


Figure 1. UV–vis spectra (left, concentration 1.0×10^{-6} M in THF at 25 °C) and the fluorescent spectra (right, concentration 1.0×10^{-6} M in THF at 25 °C, excitation at 460 nm) for poly(9,9-di-*n*-octylfluorene-2,7-vinylene)s (PFVs) containing various end groups.

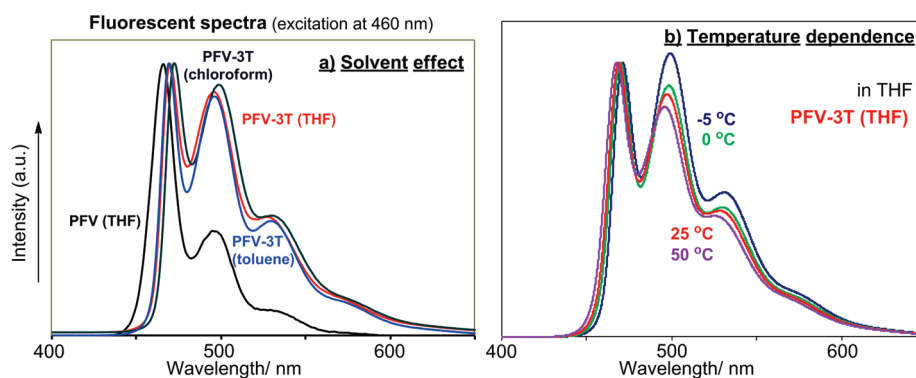


Figure 2. Fluorescent spectra in (a) various solvents (concentration 1.0×10^{-6} M at 25 °C) and (b) at various temperatures (concentration 1.0×10^{-6} M in THF), excitation at 460 nm) for PFV-3T [poly(9,9-di-*n*-octylfluorene-2,7-vinylene) containing three thiophene repeat units at both ends].

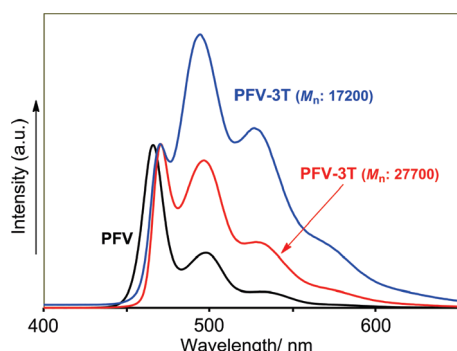


Figure 3. Fluorescent spectra of PFV-3T [poly(9,9-di-*n*-octylfluorene-2,7-vinylene) containing three thiophene repeat units at both ends] (concentration 1.0×10^{-6} M in THF, excitation at 460 nm) with different PFV repeating units ($M_n = 27\,700$ vs $17\,200$).

various temperatures (in THF at -5 to 50 °C).²⁰ Note, in contrast, the intensities at ca. 500 and 530 nm in PFV-3T were affected by the M_n value of the original PFV (Figure 3, degree of repeating units of the fluorene-2,7-vinylene, conjugation length). Moreover, the spectra were not dependent upon the excitation wavelength.²⁰

Taking into account the above facts, the unique fluorescence spectra observed by PFV-3T, PFV-MP3T, and PFV-DH4T are assumed to be ascribed as due to an energy transfer from the PFV conjugated main chain to the oligo(thiophene) moieties [not due to aggregation of rather planar oligo(thiophene) moieties];^{15,16} three or four repeating units seems to be favored than two (PFV-2T) or longer repeating units (PFV-6T).²³ Table 2 summarizes fluorescence life times estimated on the basis of fitting curves for fluorescence decays measured in THF (at 25 °C).²⁰ It should also be noted that the fluorescence life times ($\lambda_{em} = 530\text{--}609$ nm in THF) in PFV-3T, PFV-MP3T, and PFV-DH4T ($\tau = 0.654$, 0.746 , and 0.697 ns, respectively) are longer than those in the others (PFV, PFV-2T: 0.521 , 0.534 ns, respectively).²⁰

We have shown that various end-functionalized PFVs have been prepared and identified and that the PFVs containing 3 or 4 thiophene repeat units at the chain ends showed remarkable differences in the intensities at ca. 500 and 530 nm from the other samples due to an energy transfer from the PFV to the oligo(thiophene). The control of end groups in conjugated oligomers, especially a donor on one side and an acceptor on another side, has

Table 2. Fluorescence Lifetimes of Thiophene-Functionalized PFVs ($\lambda_{em} = 530\text{--}609$ nm)^a

PFV-Ar	τ /ns	PFV-Ar	τ /ns
PFV	0.521	PFV-MP3T	0.746
PFV-2T	0.534	PFV-DH4T	0.697
PFV-3T	0.654		

^a Measured in THF with a concentration of 1.0×10^{-6} M with 395–405 nm excitation in range of 5 ns at 25 °C. Detailed results are shown in the Supporting Information.²⁰

been widely investigated for photoelectron transfer studies as well as for nonlinear optics.^{18,24} In contrast, precise and total end functionalization of conjugated polymers has never been successful so far.^{15,16} As far as we know, this is the first example not only for the precise synthesis of end-functionalized conjugated polymers but also for demonstration that the emission properties in the conjugated polymers can be modified by introduction of functionality at the chain ends. We are currently expanding the chemistry including other possibilities by the end functionalization.

EXPERIMENTAL SECTION

General Procedure. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. All chemicals used were of reagent grades and were purified by the standard purification procedures. Anhydrous grade toluene (Kanto Kagaku Chemical Co., Inc.) was transferred into a bottle containing molecular sieves (mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox, stored over sodium/potassium alloy in the drybox, and then passed through an alumina short column prior to use. Anhydrous grade dichloromethane, tetrahydrofuran (THF), DMF (Kanto Kagaku Chemical Co., Inc.), and 1,2-dimethoxyethane (Aldrich Chemical Co.) were also transferred into a bottle containing molecular sieves (mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox. Mo(N-2,6-Me₂C₆H₃)(CHCMe₂Ph)[OCMe(CF₃)₂] (**Mo**)²⁵ was prepared according to the literature, and RuCl₂(PCy₃)(IMesH₂)-(CHPh) [**Ru**, Cy = cyclohexyl, IMesH₂ = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene] (Strem Chemicals, Inc.) was used in the drybox as received without further purification. Polymerization grade of 2,7-divinyl-9,9-di-*n*-octylfluorene was prepared according to the previous report.^{8,9,12} Thianaphthene-3-carboxaldehyde (**TN-CHO**), 6-(2-thienyl)-2-pyridinecarboxaldehyde (**TP-CHO**), 2,2'-bithiophene-5-carboxaldehyde (**2T-CHO**), and 2,2':5',2''-terthiophene-5-carboxaldehyde (**3T-CHO**) were used in the drybox as received

(Aldrich Chemical Co.) without further purification. 5''-Bromo-2,2':5',2''-terthiophene-5-carboxaldehyde, 2,4,6-trimethoxyphenylboronic acid neopentyl glycol ester, 3,3'''-dihexyl-2,2':5',2'':5'',2'''-quaterthiophene, α -sexithiophene, and phosphorus oxychloride were also used in the drybox as received (Aldrich Chemical Co.) without further purification.

All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^1H ; 100.40 MHz, ^{13}C), and all chemical shifts are given in ppm and are referenced to SiMe_4 . Obvious multiplicities and routine coupling constants are usually not listed, and all spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Molecular weights and the molecular weight distributions of the resultant polymers were measured by gel-permeation chromatography (GPC). HPLC grade THF was used for GPC and was degassed prior to use. GPC were performed at 40 °C on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Co. Ltd.) in THF (containing 0.03 wt % of 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns (ShimPAC GPC-806, 804, and 802, 30 cm \times 8.0 mm diameter, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from $<10^2$ to 2×10^7 MW) were calibrated versus polystyrene standard samples. UV-vis spectra for the resultant polymers were measured by using a Jasco V-550 UV/vis spectrophotometer (ex. 1.0×10^{-6} M in THF at 25 °C), and the fluorescence spectra were measured by an Hitachi F-4500 fluorescence spectrophotometer (ex. 1.0×10^{-6} M in THF at 25 °C) with excitation wavelength at 460, 430, and 410 nm. Measurements of fluorescence lifetime (1.0×10^{-6} M in THF at 25 °C) were conducted by using a Picosecond fluorescence measurement system (Hamamatsu Photonics K. K.) with Spectra Pro 2300i imaging spectrographs and monochromators (Nippon Roper K. K.).

Polymerization Procedure: Synthesis of Poly(9,9-di-*n*-octylfluorene-2,7-vinylene) (PFV) by $\text{RuCl}_2(\text{PCy}_3)(\text{IMesH}_2)(\text{CHPh})$. The polymerization procedure employed (Table 1) was analogous to those reported previously.^{8,9} Toluene (1.0 mL), 2,7-divinyl-9,9-di-*n*-octylfluorene (80 mg, 180.7 μmol), and $\text{RuCl}_2(\text{PCy}_3)(\text{IMesH}_2)(\text{CHPh})$ [Ru , 4.6 μmol] were charged into a sealed Schlenk-type tube equipped with Kontes high-vacuum valves in the drybox. The tube was then placed into a liquid nitrogen bath and was then connected to the vacuum line for a while.^{8,9} The tube was then placed into an oil bath preheated at the prescribed temperature under a reduced pressure, and the mixture was stirred for 3 h. During the reaction, the mixture was placed into a liquid nitrogen bath with a certain period [every 10 min at the initial 1 h, then every 30 min for 1 h, and then every 1 h] to remove ethylene from the reaction medium by opening the valve connected to the vacuum line and then placed into the oil bath to continue the reaction. The polymerization was quenched by adding ethyl vinyl ether in excess amount. The reaction mixture was then stirred for 1 h for completion. The resultant solution was poured into cold methanol (ca. 50 mL) and precipitated for 10 min at 5000 rpm. The yellow polymer was collected with 0.45 μm membrane filter and was then dried *in vacuo*. Yield >99%. Samples for the end functionalized ($M_n = 26\,000$, $M_w/M_n = 1.96$) were prepared by repeated experimental runs; the low molecular weight polymer sample ($M_n = 16\,700$, $M_w/M_n = 2.19$) was prepared by terminating the reaction after 1 h. ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, tetrachloroethane- d_4 , at 25 °C): δ 7.67 (br, 2H), 7.51 (br s, 4H), 7.26 (br s, 2H, *trans*-CH=CH-), 2.00 (br), 1.8 (br), 1.23 (br s), 1.09 (br s), 0.85 (br s). In addition, resonances at δ 6.82 (dd), 5.82 (d), and 5.27 (d) ppm were observed. ^1H NMR (CDCl_3 at 25 °C): δ 7.67 (d, 2H, $J = 7.2$ Hz), 7.72 (br, 4H), 7.27 (br, 2H, *trans*-CH=CH-), 6.82 (dd), 5.82 (d), 5.27 (d), 2.03 (br, 4H), 1.18–1.07 (br, 20H), 0.79 (t, 6H, $J = 6.4$ Hz, CH₃), 0.66 (br, 4H). ^{13}C NMR (CD_2Cl_4 at 25 °C): δ 151.8, 140.8, 136.4, 125.9, 120.9, 120.2, 55.1, 40.5, 32.1, 31.8, 30.3, 29.5, 24.0, 22.9, 14.4. ^{13}C NMR (CDCl_3 at 25 °C): δ 14.1, 15.7, 22.6, 23.8, 29.3, 30.1, 31.8, 40.8, 55.1, 120.0, 120.6, 125.8, 128.6, 136.5, 140.6, 151.6.

Synthesis of 5''-(2,4,6-Trimethoxyphenyl)-2,2':5',2''-terthiophene-5-carboxaldehyde (MP3T-CHO).²⁶ Into a 1,2-dimethoxyethane (25 mL) solution containing $\text{Pd}(\text{PPh}_3)_4$ (80 mg, 70 μmol) under a nitrogen atmosphere, 5''-bromo-2,2':5',2''-terthiophene-5-carboxaldehyde (178 mg, 500 μmol), aqueous K_2CO_3 (1.0 mL, 2M,

2.0 mmol), and 2,4,6-trimethoxyphenylboronic acid neopentyl glycol ester (140 mg, 528 μmol) were added. The reaction mixture was then heated to reflux for 15 h. The mixture was extracted by CH_2Cl_2 (3 \times 30 mL), and the organic layer was collected and evaporated *in vacuo*. The residue was subjected to a column chromatography (silica gel, *n*-hexane:ethyl acetate = 8:2 as eluent) to give the target compound (MP3T-CHO) as orange solids. Yield 49 mg (22%). ^1H NMR (CDCl_3): δ 9.85 (s, 1H), 7.67 (d, 1H, $J = 3.6$ Hz), 7.35 (d, 1H, $J = 3.6$ Hz), 7.28 (d, 1H, $J = 4.0$ Hz), 7.23 (d, 1H, $J = 4.0$ Hz), 7.20 (d, 1H, $J = 4.0$ Hz), 7.12 (d, 1H, $J = 3.6$ Hz), 6.23 (s, 2H), 3.87 (s, 9H). ^{13}C NMR (CDCl_3): δ 182.5, 160.9, 158.7, 147.4, 141.4, 140.3, 137.6, 135.3, 135.2, 133.8, 129.2, 127.2, 124.0, 123.9, 123.9, 105.1, 91.2, 56.1, 55.6. MS (MALDI, matrix: dithranol): calcd: 442.04; found: 442.05.

Synthesis of 3,3'''-Dihexyl-2,2':5',2'':5'',2'''-quaterthiophene-5-carboxaldehyde (DH4T-CHO).²⁷ DMF (111.9 mg, 1.53 mmol) was added into a solution of 3,3'''-dihexyl-2,2':5',2'':5'',2'''-quaterthiophene (700 mg, 1.40 mmol) in 1,2-dichloroethane (7.0 mL). Phosphorus oxychloride (234.6 mg, 1.53 mmol) was added slowly at 0 °C, and the mixture was then stirred at 40 °C for 12 h. The reaction mixture was extracted by CHCl_3 , and the extract was washed with water and dried over MgSO_4 . After removal of solvent *in vacuo*, the residue was purified by column chromatography (silica gel, hexane: CHCl_3 = 1:1 as eluent) and was then recrystallized from hexane– CHCl_3 to give orange solids of DH4T-CHO. Yield 251 mg (34%). ^1H NMR (CDCl_3): δ 9.83 (s, 1H), 7.56 (s, 1H), 7.12–7.18 (m, 4H), 7.03 (d, 1H, $J = 3.6$ Hz), 6.94 (d, 1H, $J = 5.2$ Hz), 2.76–2.82 (m, 4H), 1.62–1.72 (m, 4H), 1.32–1.42 (m, 12H), 0.89–0.94 (m, 6H). ^{13}C NMR (CDCl_3): δ 182.4, 140.9, 140.3, 140.2, 140.0, 139.1, 139.0, 136.3, 135.9, 133.7, 130.2, 130.1, 128.2, 126.5, 124.6, 124.1, 124.0, 31.7, 31.7, 30.6, 30.2, 29.5, 29.4, 29.3, 29.2, 22.7, 22.7, 14.2, 14.2.

Synthesis of α -Sexithiophene-5-carboxaldehyde (6T-CHO).²⁶ Phosphorus oxychloride (64 mg, 420 μmol) was slowly added into a 1,2-dichloroethane solution (509 mg) containing DMF (38 mg, 517 μmol). The mixture was stirred at 25 °C for 1 h. A 1,2-dichloroethane solution (509 mg) containing α -sexithiophene (200 mg, 404 μmol) was then added slowly into the mixture, and the solution was stirred at 25 °C for 1 h and was then stirred for an additional 12 h at 80 °C. The reaction mixture was poured into water (50 mL) and stirred for 2 h. Filtrated residue was dissolved in THF and precipitated in hexane to give dark red powder of 6T-CHO. Yield 118 mg (56%). In addition, it was found that resultant solid was a mixture of 6T-CHO and starting material α -sexithiophene by following analyses. But the mixture was used without further purification, because 6T-CHO and α -sexithiophene have poor solubility. ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$): δ 9.85 (s, 1H), 8.32 (s, 2H), 7.72 (m, 1H), 7.10–7.35 (m, 5H). ^1H NMR (CDCl_3): δ 9.88 (s), 8.30 (s), 7.69 (s), 7.15–7.40 (m). ^{13}C NMR (CDCl_3): δ 184.77, 124.03, 123.42, 117.30, 116.75, 116.44, 116.14. IR (KBr, cm^{-1}): 3062 ($\nu_{\text{C}=\text{H}}$), 1665 ($\text{C}=\text{O}$), 1442, 1219, 1069, 793, 457 (thiophene rings). MS (MALDI, matrix: 2,5-dihydroxybenzoic acid): calcd: 521.94; found: 522.10.

End Functionalization of PFV by $\text{Mo}(\text{N},2,6\text{-Me}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})[\text{OCMe}(\text{CF}_3)_2]$.⁸ The experimental procedure was analogous to that reported previously.⁸ Into a stirred toluene solution (2.5 mL) containing poly(2,7-divinyl-9,9-di-*n*-octylfluorene) (PFV, 50 mg), a toluene solution (0.5 mL) containing $\text{Mo}(\text{N},2,6\text{-Me}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})[\text{OCMe}(\text{CF}_3)_2]_2$ [Mo , 3.6–4.7 equiv] was added at room temperature, and the solution was stirred for 2 h. The solution was then added prescribed aldehyde ($\text{Ar}-\text{CHO}$) in excess amount (>5.43 equiv to Mo) and was stirred for an additional 1 h for completion. The solution was then poured dropwise into methanol, and the precipitated samples were collected by centrifuge for 10 min at 5000 rpm. The yellow polymer, PFV-Ar, was collected on a 0.45 μm membrane filter and was then dried *in vacuo*. PFVs for this reaction were dissolved in toluene in the drybox, the solution was passed through a

Celite pad, and the filtrate was dried *in vacuo*; the process is required to remove oxygen and water contaminant in the polymer samples (because the molybdenum catalyst is highly sensitive to the impurities).

PFV-TP. Yield: 98%. ^1H NMR (CDCl_3) δ : [7.00–8.00, thienylpyridine], 7.68 (d, 2H, $J = 8.1$ Hz), 7.52 (br, 4H), 7.27 (br, 2H), 2.04 (br, 4H), 1.15 (m, 20H), 0.79 (t, 6H, $J = 7.0$ Hz), 0.66 (br, 4H).

PFV-TN. Yield: 98.0%. ^1H NMR (CDCl_3) δ : [7.00–8.00, thianaphthene], 7.68 (d, 2H, $J = 8.1$ Hz), 7.52 (br, 4H), 7.27 (br, 2H), 2.04 (br, 4H), 1.15 (m, 20H), 0.79 (t, 6H, $J = 7.0$ Hz), 0.66 (br, 4H).

PFV-2T. Yield: 96%. ^1H NMR (CDCl_3) δ : [7.00–7.50, bithiophene], 7.68 (d, 2H, $J = 8.1$ Hz), 7.52 (br, 4H), 7.27 (br, 2H), 2.04 (br, 4H), 1.15 (m, 20H), 0.79 (t, 6H, $J = 7.0$ Hz), 0.66 (br, 4H).

PFV-3T. Yield: >99%. ^1H NMR (CDCl_3) δ : [6.20–7.20, terthiophene], 7.68 (d, 2H, $J = 8.1$ Hz), 7.52 (br, 4H), 7.27 (br, 2H), 2.04 (br, 4H), 1.15 (m, 20H), 0.79 (t, 6H, $J = 7.0$ Hz), 0.66 (br, 4H).

PFV-MP3T. Yield: >99%. ^1H NMR (CDCl_3) δ : [6.90–7.50, 6,24 (bs), 3.86 (bs), trimethoxyphenylterthiophene], 7.68 (d, 2H, $J = 8.1$ Hz), 7.52 (br, 4H), 7.27 (br, 2H), 2.04 (br, 4H), 1.15 (m, 20H), 0.79 (t, 6H, $J = 7.0$ Hz), 0.66 (br, 4H).

PFV-DH4T. Yield: >99% (after precipitation in methanol). After precipitation, the precipitate was dissolved in a small amount of CHCl_3 and reprecipitated in hexane for further purification. Yield: 34 mg (68%). ^1H NMR (CDCl_3) δ : [6.96–7.22, 2.80, 1.45, 0.93, dihexylquarterthiophene], 7.68 (d, 2H, $J = 8.1$ Hz), 7.52 (br, 4H), 7.27 (br, 2H), 2.04 (br, 4H), 1.15 (m, 20H), 0.79 (t, 6H, $J = 7.0$ Hz), 0.66 (br, 4H).

PFV-6T. Yield: >99% (after precipitation in methanol). 30 mg of PFV was used for this reaction. After precipitation, precipitate was dissolved in CHCl_3 and filtered with glass filter, and the filtrate was evaporated *in vacuo*. The resultant polymer was then dissolved in THF and reprecipitated in hexane for further purification. Yield: 12 mg (40%). ^1H NMR (CDCl_3) δ : [7.00 (bs, 6H), 6.86 (s, 2H), 6.61 (d, $J = 12.0$ Hz, 1H), 6.50 (s, 3H), 6.02 (d, $J = 12.8$ Hz, 1H) sexithiophene], 7.68 (d, 2H, $J = 8.1$ Hz), 7.52 (br, 4H), 7.27 (br, 2H), 2.04 (br, 4H), 1.15 (m, 20H), 0.79 (t, 6H, $J = 7.0$ Hz), 0.66 (br, 4H).

■ ASSOCIATED CONTENT

Supporting Information. ^1H NMR spectra (in CDCl_3 at 25 °C) for poly(fluorene-2,7-vinylene)s containing functional groups at the chain ends, UV–vis and fluorescence spectra for poly(fluorene-2,7-vinylene)s, and fluorescence decays for poly(fluorene-2,7-vinylene)s (1.0×10^{-6} M in THF). This material is available free of charge via Internet at <http://pubs.acs.org>.

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(19) Samples (PFVs) for the subsequent reactions were prepared by repeating the same procedure and both M_n and M_w/M_n values were average in the several experimental runs (values in the mixtures).

(20) ^1H NMR spectra and UV–vis and their fluorescence spectra are shown in the Supporting Information.

(21) As reported previously,⁷ the M_n value in GPC vs polystyrene standards is higher than that in GPC vs PPP standards because of the nature of rigid conjugated polymers, and the estimation [$M_{n(\text{calcd})} = M_{n(\text{GPC})}/1.6$] was adopted for further study.^{8,9}

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