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ARTICLE TYPE

Precise One-Pot Synthesis of Fully Conjugated End-Functionalized Star Polymers Containing Poly(fluorene-2,7-vinylene) (PFV) Arms

Kotohiro Nomura,^{*,a,b} Tahmina Haque,^a Tomohiro Miwata,^a Akiko Inagaki,^a Kenji Takamizu^a

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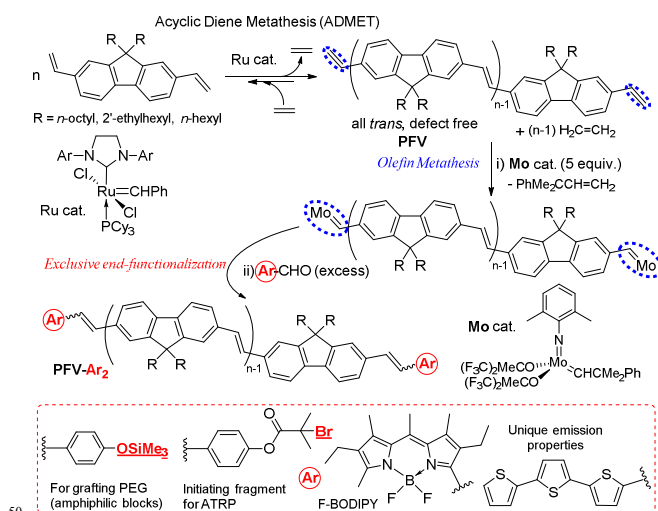
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A facile, precise one-pot synthesis of end-functionalized star (triarm) polymers consisting of poly(9,9-di-*n*-octylfluorene-2,7-vinylene)s (PFVs), the triblock copolymers [by incorporation of tri(2,5-dialkoxy-1,4-phenylene vinylene) or terthiophene units as the middle segment], have been prepared by olefin metathesis followed by Wittig-type coupling; effect of PFV conjugation length, middle segment and the end groups toward the emission properties have been studied.

Introduction

Organic electronics are important emerging technologies, and conjugated polymers are of continuing interest as a result of their applications in optoelectronic and electrochemical devices. Synthesis of structurally regular, chemically pure conjugated polymers by development of new synthetic methods attracts considerable attention,¹ because their performances (in optoelectronic, electrochemical devices) are affected by the structural regularity, chemical purity, and supramolecular order.^{2,3} Moreover, formation of regular one-dimensional conjugated structures on the nano-scale should be expected by exploiting the specific assembling properties of rod-coil block copolymers;^{4,5} the end-group modification has also been promising for better unique properties (via energy transfer etc.).⁶⁻⁸ Although monodisperse star-shaped conjugated oligomers (dendrimers, star molecules)⁹ are known to exhibit unique properties (well-defined chemical structure, better mechanical properties and solubility in organic solvents) in organic light-emitting devices,^{9r,10} reports concerning precise synthesis of fully conjugated star polymers have been limited so far.¹¹ This is probably due to a difficulty of an exclusive introduction of the side arm into the core (via multi-terminator or grafting to approach) and/or precise propagations (via multi-initiator or grafting from approach) from the core molecules. We demonstrated syntheses of *defect-free*, stereo-regular (*all-trans*), high molecular weight poly(9,9-dialkylfluorene-2,7-vinylene)s (PFVs), poly(2,5-dialkyl-phenylene-1,4-vinylene)s by acyclic diene metathesis (ADMET) polymerization.¹²⁻¹⁶ Since the resultant polymers prepared by Ru-carbene catalyst possessed well-defined polymer chain ends (as vinyl group),^{12b,13,15} a facile and exclusive end-functionalization can be achieved by treating the vinyl groups with Mo(CHCMe₂Ph)(N-2,6-Me₂C₆H₃)[OCMe(CF₃)₂]₂ (**Mo** cat.) followed by Wittig-type cleavage with aldehyde.^{13,17,18} Various end functionalities such as oligo-(thiophene)s,^{13b} initiating fragment for atom transfer radical polymerization (ATRP),^{13c} and chromophores,^{13d} can be achieved

by adopting this methodology (Scheme 1). Moreover, the method enables us for one-pot synthesis of end-functionalized conjugated multi-block copolymers in a precise manner.^{13e}



Scheme 1. Synthesis of poly(9,9-di-*n*-octyl-fluorene-2,7-vinylene)s (PFVs) with well-defined end groups.

In this paper, we thus wish to present a facile, precise one-pot synthesis of fully conjugated end-functionalized star-shaped polymers by adopting a combined olefin metathesis and the subsequent Wittig-type coupling.¹⁹ We also present that the method enables us one-pot synthesis of end-functionalized conjugated multi-block copolymers in a precise manner.

Results and Discussion

1. Synthesis of end-functionalized star shaped polymers by a combined olefin metathesis and subsequent Wittig coupling.

Poly(9,9-di-*n*-octyl-fluorene-2,7-vinylene)s (PFVs) prepared by the ADMET polymerization using Ru catalyst have been chosen, not only because, as described above, the method affords

defect-free, all-trans polymers with well-defined chain ends (vinyl group),^{12b,13} but also because various end functionalities can be introduced exclusively by treating the vinyl end groups^{12b,13,14} with Mo catalyst/reagent, followed by Wittig-type cleavage.^{13,18,19} PFVs with different M_n values (Table 1) were prepared by varying the reaction time and/or the subsequent fractional separation,^{13e,20,21} to explore an effect of conjugation length toward the optical properties (described below).^{13e}

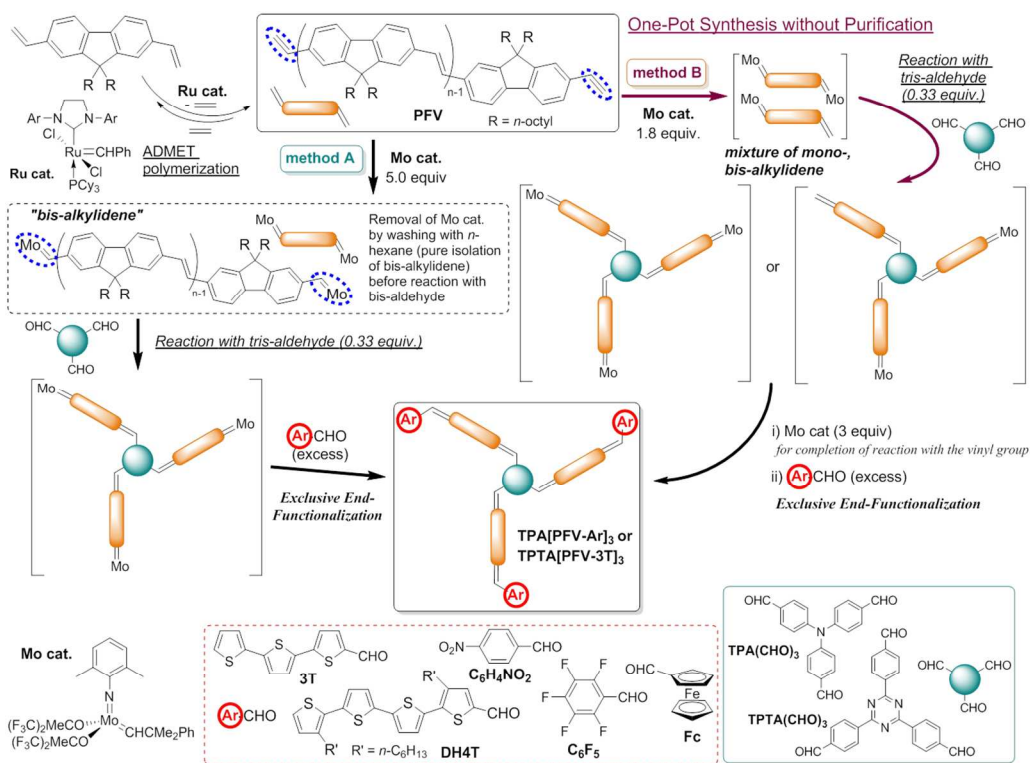
Two approaches shown in Scheme 2 have been considered for this purpose.^{13e} In method A, the vinyl groups in the PFVs' chain ends were treated with Mo catalyst/reagent (5 equiv) to afford the "bis-alkylidene" species *in situ*.²² The species, were isolated *in situ* by washing with cold *n*-hexane for removal of the residual Mo catalyst/reagent (with the aid of a difference in solubility). The resultant polymer precipitates were then dissolved in toluene and the solution was added a CH₂Cl₂ solution containing 2,4,6-tris(4-formylphenyl)amine or 2,4,6-tris(4-formylphenyl)-1,3,5-triazine [expressed as TPA(CHO)₃, TPTA(CHO)₃, respectively, 1/3 equiv of PFV]. The stirred mixture was then added prescribed aldehyde (ArCHO) in excess amount for the end functionalization. The resultant star polymers were isolated simply by pouring the reaction mixture into methanol (39-75% yields on the basis of PFVs, Table 1, runs 1-7).²⁰

The M_n values in the resultant polymers, TPA-[PFV-Ar]₃ [Ar = C₆F₅, 4-C₆H₄NO₂, 3,3''-dihexyl-2,2':5',2'': 5'',2''-quarterthiophene (DH4T), 2,2':5',2''-terthiophene (3T)], estimated by GPC (*vs* polystyrene standards) are analogous to those on the basis of starting PFV samples, and the molecular weight distributions observed by GPC traces were unimodal ($M_w/M_n = 1.64-2.28$).²² The polymers were also identified by ¹H NMR spectra,²⁰ and resonances ascribed to protons of the vinyl groups in the starting PFVs were not observed. Note that the estimated

M_n value on the basis of integration in TPA[PFV-Fc]₃ (using protons in the Fc, expressed as $M_{n(NMR)}$ in Table 1, run 7) was relatively close to that calculated on the basis of molar ratios, suggesting an exclusive formation of the desired polymer. The reaction with TPTA-(CHO)₃ in place of TPA(CHO)₃ afforded TPTA[PFV-3T]₃ with unimodal molecular weight distributions ($M_w/M_n = 2.19$).

Since the above method requires a purification/isolation step of the "bis-alkylidene" species, another approach (method B)^{13e} has been considered to explore a possibility of more facile "one-pot" method for the synthesis. The vinyl groups in the PFVs' chain ends were treated with Mo cat. (1.8 equiv to PFV, for complete conversion of Mo *in situ*), and the mixture was then added a CH₂Cl₂ solution containing TPA(CHO)₃. The reaction mixture was added a toluene solution containing Mo cat (3 equiv) for completion of the olefin metathesis, and the subsequent addition of aldehyde (ArCHO) in excess amount afforded the end-functionalized star (triarm) copolymers, TPA[PFV-Ar]₃ [Ar = C₆F₅, ferrocene (Fc)].

The M_n values in the resultant polymers estimated by GPC, are analogous to those on the basis of starting PFV samples; the molecular weight distributions were uniform (runs 8-13, Table 1).²² Resonances ascribed to protons in Fc moiety in TPA[PFV-Fc]₃ in the ¹H NMR spectra were clearly observed,²⁰ whereas resonances ascribed to protons of the vinyl groups in the starting PFVs were diminished.²⁰ Note that the estimated M_n values on the basis of integration in TPA[PFV-Fc]₃ were highly analogous to those calculated on the basis of molar ratios, suggesting an exclusive formation of end-functionalized star polymers, TPA[PFV-Ar]₃. The latter one-pot method (method B) should be promising and useful, because the target star polymers can be easily prepared in a precise manner without purification.



Scheme 2. Two approaches for synthesis of end-functionalized conjugated (triarm) star polymers adopted in this study.

Table 1. Synthesis of triblock copolymers with well-defined end functional groups.

run	polymers	PFV ^a			method	polymer			yield ^f / %	
		$M_n(\text{GPC})^b$	M_w/M_n^b	$M_n(\text{calcd})^c$		A or B	$M_n(\text{GPC})^b$	$M_n(\text{calcd})^d$		$M_n(\text{NMR})^e$
1	TPA[PFV-C ₆ F ₅] ₃	9400	1.83	5880	A	38000	18200		2.28	75
2	TPA[PFV-C ₆ F ₅] ₃	10400	1.75	6500	A	39900	20100		1.64	52
3	TPA[PFV-C ₆ H ₄ NO ₂] ₃	8000	1.79	5000	A	25400	15600		1.81	39
4	TPA[PFV-DH4T] ₃	10700	2.12	6690	A	38300	21800		1.94	46
5	TPA[PFV-3T] ₃	8100	1.94	5060	A	24900	16200		1.93	47
6	TPTA[PFV-3T] ₃	11300	1.95	7060	A	35300	22300		2.19	52
7	TPA[PFV-Fc] ₃	5500	1.84	3440	A	17200	11200	12600	2.26	47
8	TPA[PFV-C ₆ F ₅] ₃	13400	2.00	8370	B	35500	25700		2.06	70
9	TPA[PFV-C ₆ F ₅] ₃	19900	1.80	12400	B	44700	37800		1.68	72
10	TPA[PFV-Fc] ₃	8400	1.90	5250	B	22100	16600	16300	1.40	64
11	TPA[PFV-Fc] ₃	9230	1.11	5760	B	20700	18100	17400	1.22	66
12	TPA[PFV-Fc] ₃	18000	1.67	11300	B	35000	34800	33600	1.48	22
13	TPA[PFV-Fc] ₃	19900	1.80	12400	B	46700	38100		1.50	68

^a PFV employed for the syntheses. ²⁰ ^b GPC data in THF vs polystyrene standards. ^c $M_n(\text{calcd}) = M_n(\text{GPC})/1.6$, according reference 21. ^d Calculated on the basis of molar ratio. ^e Estimated by the integration ratio (end groups). ^f Isolated yield.

Based on the above facts and our previous report,^{13e} *one-pot* syntheses of the end-functionalized star polymers containing conjugated block copolymers, expressed as TPA[$\{(PFV)_2\text{-}3PV\}\text{-Ar}\}_3$ or TPA[$\{(PFV)_2\text{-}3T\}\text{-Ar}\}_3$ (Ar = C₆F₅, Fc) were explored (Scheme 3). The vinyl groups in the PFVs' chain ends were treated with Mo cat. (1.8 equiv to PFV), and the mixture was then added a CH₂Cl₂ solution containing 0.5 equiv of 3PVCHO or 3T(CHO)₂. The solution was further added a CH₂Cl₂ solution containing TPA(CHO)₃ (1/6 equiv to PFV) for formation of the triarm core, and was then added a toluene solution containing Mo cat (3 equiv) to complete the olefin metathesis. The subsequent addition of aldehyde (ArCHO) in excess amount afforded the targeted end-functionalized triarm polymers containing conjugated triblock copolymers as the arm segment (40-93% yields on the basis of PFVs, Table 2), which were isolated simply by pouring the mixture into MeOH.

The M_n values in the resultant polymers were analogous to the estimated values with the unimodal distributions ($M_w/M_n = 1.19\text{-}1.32$, Table 2). In the ¹H NMR spectra,²⁰ resonances ascribed to protons in Fc (and 3PV) moiety were clearly observed, whereas resonances ascribed to protons of the vinyl groups (in the starting PFVs) were not observed. Note that the estimated M_n values on the basis of integration (using protons in the Fc and 3PV) were highly analogous to the calculated values on the basis of molar ratios. The results also suggest an exclusive formation of end-functionalized star polymers containing triblock copolymers.

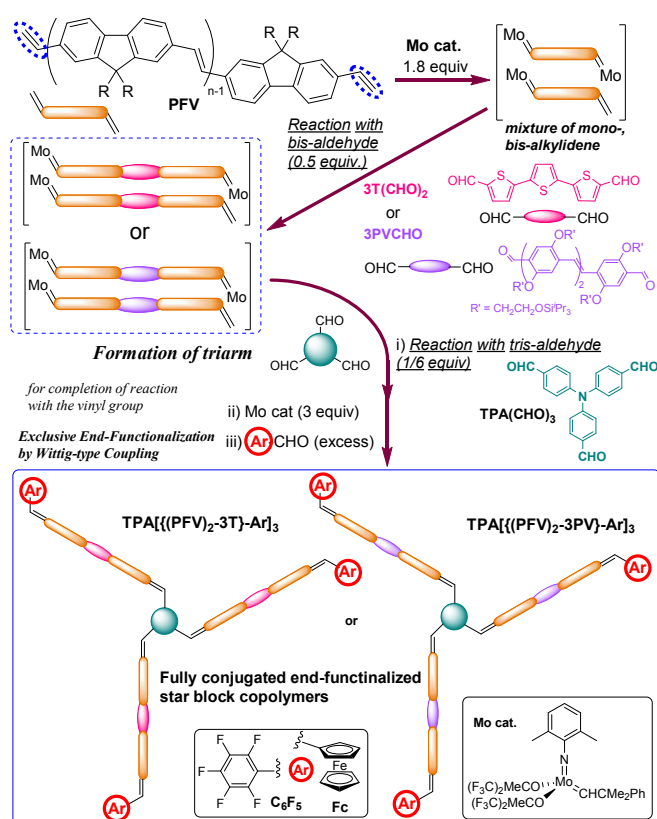
**Scheme 3.** Synthesis of end-functionalized (triarm) star polymers containing conjugated triblock copolymers.

Table 2. Synthesis of end-functionalized (triarm) star polymers containing conjugated triblock copolymers.^a

run	polymers	$M_n(\text{GPC})^b$	$M_n(\text{calcd})^c$	$M_n(\text{NMR})^d$	M_w/M_n^e	yield ^e / %
14	TPA[$\{(PFV)_2\text{-}3PV\}\text{-}C_6F_5\}_3$	48100	26100	(26700)	1.27	69
15	TPA[$\{(PFV)_2\text{-}3PV\}\text{-}Fc\}_3$	46900	26400	26700	1.19	40
16	TPA[$\{(PFV)_2\text{-}3T\}\text{-}C_6F_5\}_3$	51700	25300	--	1.32	93
17	TPA[$\{(PFV)_2\text{-}3T\}\text{-}Fc\}_3$	41200	25600	22700	1.2	67

^a PFV employed for the syntheses: $M_n(\text{GPC}) = 6380$, $M_n(\text{calcd}) = 3990$ [$M_n(\text{GPC})/1.6$],²¹ $M_n(\text{NMR}) = 3500$ (estimated by the integration with the vinyl group in the ¹H NMR spectrum), $M_w/M_n = 1.99$. ^b GPC data in THF vs polystyrene standards. ^c Calculated on the basis of molar ratio. ^d Estimated by the integration ratio (middle and/or end groups). ^e Isolated yield. ^f Confirmed formation of the triblock copolymers by integration ratio of PFV and 3PV.

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2. UV-vis and fluorescence spectra in the end-functionalized (triblock) star polymers.

UV-vis spectra (in THF at 25 °C, conc. 1.0×10^{-6} M, Figure 1) for TPA[(PFV)-Ar]₃ (Ar = C₆F₅, 4-NO₂C₆H₄, 3T, DH4T, Fc) and TPTA[(PFV)-3T]₃ displays two absorption bands at 455, 427 (and 400) nm, that can be ascribed to $\pi\text{-}\pi^*$ transitions (0-0, 0-1, and 0-2 transitions, respectively) of the conjugated backbone.^{13b,e,23} No significant differences in the spectra with the original PFV (before modification) were observed even by varying the end groups.¹³ The absorbance in the λ_{max} increased upon increasing the M_n values,²⁴ because the rather low molecular weight PFV samples contain oligomers with less than effective conjugation length (Figure 2),^{13e,25} as assumed previously.^{13e} Moreover, remarkable differences in both the λ_{max} values and their absorbance were not observed in TPA[$\{(PFV)_2\text{-}3PV\}\text{-}Ar\}_3$ and TPA[$\{(PFV)_2\text{-}3T\}\text{-}Ar\}_3$ (Ar = C₆F₅, Fc) consisting of same PFV samples [$M_n(\text{calcd})$ of starting PFV = 3990, $M_w/M_n = 1.99$, run 16-19, Figure 2b].

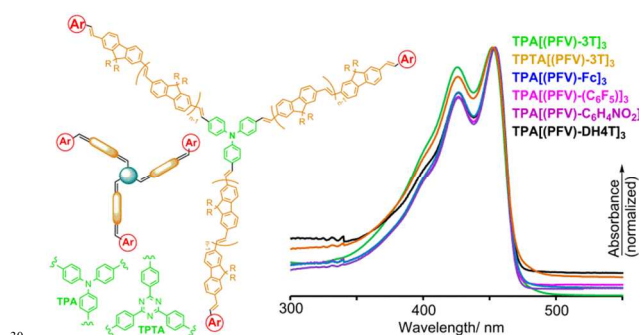


Figure 1. UV-vis spectra (in THF at 25 °C, conc. 1.0×10^{-6} M) for TPA[(PFV)-Ar]₃ [Ar = C₆F₅ ($M_n(\text{calcd}) = 18200$), 4-NO₂C₆H₄ ($M_n(\text{calcd}) = 15600$), 3T ($M_n(\text{calcd}) = 16200$), DH4T ($M_n(\text{calcd}) = 21800$), Fc ($M_n(\text{calcd}) = 11200$)], TPTA[(PFV)-3T]₃ ($M_n(\text{calcd}) = 22300$).

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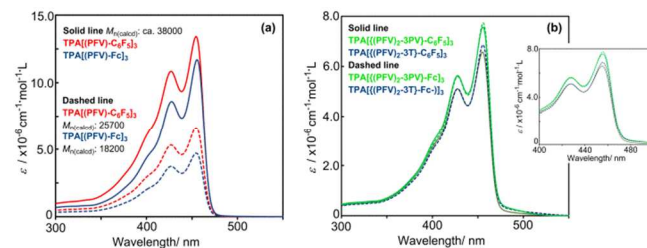


Figure 2. UV-vis spectra (in THF at 25 °C, conc. 1.0×10^{-7} M) for a) TPA[(PFV)-Ar]₃ b) TPA[$\{(PFV)_2\text{-}3PV\}\text{-}Ar\}_3$ or TPA[$\{(PFV)_2\text{-}3T\}\text{-}Ar\}_3$ (Ar = C₆F₅, Fc) with different molecular weights (conjugation repeat unit).

Figure 3 shows fluorescence spectra (in THF at 25 °C, excitation at 450 nm) for TPA[(PFV)-Ar]₃ (Ar = C₆F₅, 4-NO₂C₆H₄, 3T, DH4T) and TPTA[(PFV)-3T]₃. Corresponding emission peaks of two/three absorption bands in the UV-vis spectra were observed at 466, 497, and 530 nm (Table 3).^{13b,e,23} No significant effects of the end groups toward both the λ_{max} values and their intensities (including ratios in their intensities) were observed in the spectra of TPA[(PFV)-Ar]₃ (Ar = C₆F₅, 4-NO₂C₆H₄, DH4T). In contrast, the spectra in TPA[(PFV)-3T]₃ and TPTA[(PFV)-3T]₃ showed apparent differences in the intensities at 497 nm and 527 nm [probably due to an energy transfer from the PFV to 3T, as assumed previously by PFV-(3T)₂],^{13b} and a difference in their intensities were affected by the conjugation length.^{13b}

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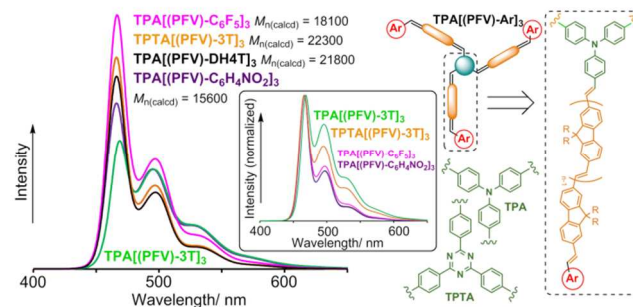


Figure 3. Fluorescence spectra (in THF at 25 °C, conc. 1.0×10^{-6} M, excitation at 450 nm) for TPA[(PFV)-Ar]₃ [Ar: C₆F₅ (run 11), 4-NO₂C₆H₄ (run 3), DH4T (run 4)], TPTA[(PFV)-3T]₃ (run 6).

Note that a placements of ferrocene (Fc) as the end group, TPA[(PFV)-Fc]₃, caused a notable quenching of photoluminescence, accompanied decreasing in the quantum yields [Figures 4a and 5, $\Phi_{\text{PL}} = 0.08$ (run 11), 0.16 (run 13), Table 3].^{13e,24,27} Decrease in the intensity (and Φ_{PL}) was affected by the PFV length, probably due to an exciton transfer to the Fc units.^{24e,27} The Φ_{PL} value as well as intensity in TPA[(PFV)-C₆F₅]₃ ($\Phi_{\text{PL}} = 0.67$, run 8) was also lower than PFV itself ($\Phi_{\text{PL}} = 0.89$, Figure 4b). The intensity in TPA[$\{(PFV)_2\text{-}3PV\}\text{-}C_6F_5\}_3$ or TPA[$\{(PFV)_2\text{-}3T\}\text{-}C_6F_5\}_3$ was lower than TPA[(PFV)-C₆F₅]₃, probably due to low PFV length in each blocks. Relative intensity at 528 nm in TPA[$\{(PFV)_2\text{-}3PV\}\text{-}C_6F_5\}_3$ became higher than that in TPA[$\{(PFV)_2\text{-}3T\}\text{-}C_6F_5\}_3$, due to a presence of 3PV (emission of 3PV).^{13e}

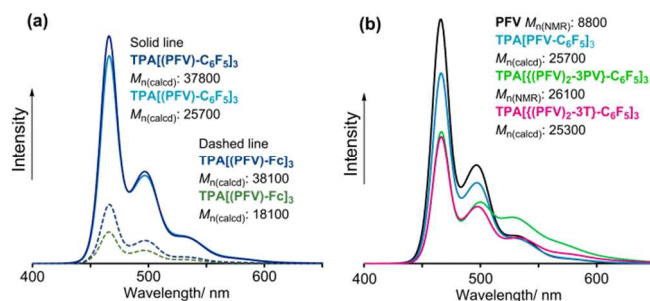


Figure 4. Fluorescence spectra (in THF at 25 °C, excitation at 450 nm, measured under absorbance at 0.1) for a) TPA[(PFV)-Ar]₃ (Ar = C₆F₅, Fc) with different molecular weights, b) TPA[{(PFV)₂-3PV}-Ar]₃ or TPA[{(PFV)₂-3T}-Ar]₃ (Ar = C₆F₅, Fc).

Figure 5 shows fluorescence spectra for the linear polymer,^{13e} the linear triblock copolymer,^{13e} and the star (block) polymers with relatively similar PFV length, and the elected optical properties are summarized in Table 3. No apparent differences in the intensities and the λ_{max} values were observed in TPA[{(PFV)₂-3PV}-C₆F₅]₃ and TPA[{(PFV)₂-3T}-C₆F₅]₃, although a slight difference in the Φ_{PL} values was observed [Φ_{PL} = 0.69 (run 14), 0.54 (run 16), respectively], as observed in the linear triblock copolymers.^{13e} A placement of Fc as the end group, TPA[{(PFV)₂-3PV}-Fc]₃ or TPA[{(PFV)₂-3T}-Fc]₃, caused a quenching of photoluminescence, accompanied by decrease in the Φ_{PL} values [Φ_{PL} = 0.26 (run 15), 0.18 (run

17)].^{13e,24,27} The relative intensities of ca. 526-530 nm (vs ca. 466 nm) in these star block copolymers were higher than that in TPA[(PFV)-Fc]₃ probably due to an emission/energy transfer (of 3PV/3T),^{13b,e} whereas the intensities at 466 nm and the Φ_{PL} values in these samples were close. The degree of quenching was also affected by the middle segment (3T or TPA)^{13e} exemplified in PFV(Fc)₂, [(PFV)₂-3T](Fc)₂, and TPA[(PFV)-Fc]₃.

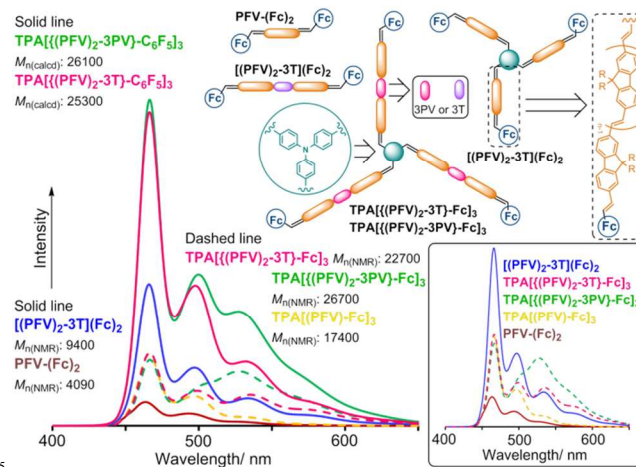


Figure 5. Fluorescence spectra for linear and star (co)polymers (in THF at 25 °C, excitation at 450 nm, measured under absorbance at 0.1, with rather low molecular weight samples).

Table S2. Summary of selected optical properties.

run	polymers	$M_{\text{n(calcd)}}^a$	$M_{\text{n(NMR)}}^b$	absorption ^c $\lambda_{\text{max}}/\text{nm}$	fluorescence ^d $\lambda_{\text{max}}/\text{nm}$	Φ_{PL}^e
8	TPA[PFV-C ₆ F ₅] ₃	25700	--	427, 455	466, 497, 530	0.67
9	TPA[PFV-C ₆ F ₅] ₃	37800	--	427, 455	466, 497, 530	0.69
11	TPA[PFV-Fc] ₃	18100	17400	427, 455	466, 497, 530	0.08
13	TPA[PFV-Fc] ₃	38100	--	428, 456	466, 497, 531	0.16
14	TPA[{(PFV) ₂ -3PV}-C ₆ F ₅] ₃	26100	--	428, 456	466, 500, 527	0.69
15	TPA[{(PFV) ₂ -3PV}-Fc] ₃	26400	26700	428, 456	466, 500, 528	0.26
16	TPA[{(PFV) ₂ -3T}-C ₆ F ₅] ₃	25300	--	428, 455	466, 498, 532	0.54
17	TPA[{(PFV) ₂ -3T}-Fc] ₃	25600	22700	428, 456	466, 499, 535	0.18
	[(PFV) ₂ -3T](C ₆ F ₅) ₂ ^f	9600	--	427, 455	466, 497, 531	0.65
	[(PFV) ₂ -3T](Fc) ₂ ^f	9700	9400	427, 455	466, 497, 533	0.20
	[(PFV) ₂ -3PV](C ₆ F ₅) ₂ ^f	9900	8900	427, 455	466, 499, 526	0.74
	[(PFV) ₂ -3PV](Fc) ₂ ^f	9900	9000	427, 455	466, 499, 526	0.16
	PFV ^f	--	--	426, 453	466, 497, 530	0.89

^aCalculated on the basis of molar ratio. ^bEstimated by NMR spectra. ^cBy UV-vis spectra (in THF, conc. 1.0×10^{-7} M, at 25 °C). ^dBy fluorescence spectra (in THF at 25 °C). ^ePhotoluminescence quantum yield (Φ_{PL}) in THF (excitation wavelength at 450 nm) at 25 °C. ^fCited from reference 13c.

Conclusion

We have shown that a precise *one pot synthesis of fully conjugated end-functionalized star polymers* containing PFV main chain has been accomplished by adopting olefin metathesis and subsequent Wittig-type coupling. The method can also be applied for synthesis of the star polymers containing triblock copolymers as the arm segment. Unique emission properties including effect of PFV length, middle segment and the end groups toward both the intensity and the photoluminescence quantum yield (Φ_{PL}) were observed, especially by placement of ferrocene moiety at the chain ends. The results presented here should be highly promising not only in terms of precise synthesis, but also of exploring effects of end groups, unique shape (star),

conjugation length and middle segment. We believe that information through this study should be highly promising for better design of materials for the desired purpose. It is clear that the method provides various modifications (main chain, core, middle segment, and end groups). We are now exploring a possibility to demonstrate unique characteristics by integration of functionality as the star full conjugated macromolecule, and the results will be introduced in the near future.

Experimental Section

General procedure.

All experiments were carried out under a nitrogen atmosphere in a vacuum atmospheres drybox or using standard Schlenk technique unless otherwise noted. All chemicals used were of

reagent grades and were purified by the standard purification procedures. Anhydrous grade toluene (Kanto 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, and was stored over sodium/potassium alloy, and was used after passing through an alumina short column under nitrogen flow prior to use. Anhydrous grade THF, dichloromethane (Kanto Chemical Co., Inc.) were also transferred into a bottle containing molecular sieves in the drybox. Mo(CHCMe₂Ph)(N-2,6-Me₂C₆H₃)[OCMe(CF₃)₂]₂ (**Mo**)²⁸ 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. Polymerization grade of 2,7-divinyl-9,9-di-*n*-octylfluorene was prepared according to the previous report.¹³ Pentafluorobenzaldehyde (C₆F₅CHO), and ferrocene carboxaldehyde were also used in the drybox as received (Sigma-Aldrich Co.) without further purification. **3PV-CHO** [tris(2,5-dialkoxy-1,4-phenylene vinylene) with CHO as the chain ends: alkoxy = OCH₂CH₂OSiⁱPr₃] was prepared according to the reported procedure.^{18a} **3T(CHO)**₂ was prepared according to the reported procedure.^{13c}

All ¹H and ¹³C NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz for ¹H, 125.77 MHz for ¹³C) and all chemical shifts are given in ppm and are referenced to SiMe₄. 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 × 8.0 mm diameter, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from < 10² to 2×10⁷ 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 (conc. 1.0×10⁻⁷ M in THF at 25 °C), and the fluorescence spectra were measured by Hitachi F-4500 fluorescence spectrophotometer (under absorbance 0.1 in THF at 25 °C) with excitation wavelength at 450 nm, and the fluorescence quantum yields were measured by Hamamatsu photonics C9920-02G (ex. under absorbance at 0.1 in THF at 25 °C) with excitation wavelength at 450 nm. Preparative gel-permeation chromatography (GPC) was performed on a YMC LC-Forte/R (YMC group) using UV detector in toluene with flow rate 10.0 mL/min, equipped with YMC-GPC T4000 and YMC-GPC T30000 columns, ranging from 4×10³ to 30×10³ MW.

Polymerization Procedure (Starting polymer sample preparation): Synthesis of poly(9,9-di-*n*-octylfluorene-2,7-vinylene) (PFV) by RuCl₂(PCy₃)(IMesH₂)(CHPh).

The polymerization procedure employed was analogous to those reported previously.¹ Toluene (1.0 mL), 2,7-divinyl-9,9-di-*n*-octylfluorene (150 mg, 339 μmol), and RuCl₂(PCy₃)(IMesH₂)(CHPh) (**Ru**, 8.5 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. The tube was then placed into an oil bath preheated at 50 °C under a reduced pressure, and the mixture was stirred for 1-5 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 by-produced 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, and 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 96 %. ¹H NMR (CDCl₃): δ 7.72 (d, 2H, *J* = 7.9 Hz), 7.54 (br, 4H), 7.29 (br, 2H, *trans*-CH=CH-), 6.81 (dd), 5.81 (d), 5.26(d), 2.05 (br, 4H), 1.17-1.08 (br, 20H), 0.87(t, *J* = 7.0 Hz, 6H), 0.68 (br, 4H). The selected data for samples prepared for the subsequent end-functionalization are shown in Table S1. The resultant PFV samples were separated into two fractions by using *n*-hexane.

Synthesis of end-functionalized star polymers, TPA[PFV-Ar]₃.

(i) Method A: Typical experimental procedure is as follows. Into a stirred toluene solution (1.0 mL) containing a solution of poly(9,9-di-*n*-octyl-fluorene-2,7-vinylene) (PFV, 20 mg) was added a toluene solution (1.0 mL) containing Mo(CHCMe₂Ph)(N-2,6-Me₂C₆H₃)[OCMe(CF₃)₂]₂ (**Mo** cat., 5.0 equiv) at room temperature and the reaction mixture was stirred for 2 h. The solution was placed *in vacuo* to remove toluene, and the unreacted **Mo** was then removed by dissolving/washing with cold *n*-hexane at least twice (because Mo catalyst is highly soluble in *n*-hexane at -30 °C) in the drybox. The resultant polymer was dried *in vacuo*, and the resultant polymer (the amount was weighted after washing with *n*-hexane and dried *in vacuo*) was dissolved in toluene (2.0 mL). Into the stirred toluene solution containing PFV connected **Mo** (*bis-alkylidene*), a dichloromethane (0.5 mL) solution containing tris(4-formylphenyl)amine [TPA(CHO)₃] (corresponds to 0.3 mg/0.5 mL-CH₂Cl₂, 1/3 equiv to PFV) and the solution was stirred for 1 h. The reaction was then terminated by adding the prescribed aldehyde (Ar-CHO) in excess amount (10 equiv to the PFV) and was stirred for an additional 1 h for completion. The resultant star conjugated polymer was then precipitated by pouring in cold methanol and was then collected by filtration after centrifuge. The star polymer was then further purified as precipitate by using chloroform and methanol. The precipitates, collected by filtration were dried *in vacuo*, affording the star polymers, TPA[PFV-Ar]₃.

(ii) Method B: Typical experimental procedure is as follows. Into a stirred toluene solution (3.0 mL) containing a solution of poly(9,9-di-*n*-octyl-fluorene-2,7-vinylene) [PFV, 30 mg, *M*_{n(calcd.)} = 12400, *M*_{n(NMR)} = 11000, 2.7 μmol, used for runs 9, 13] was added a toluene solution (1.0 mL) containing Mo(CHCMe₂Ph)(N-2,6-Me₂C₆H₃)[OCMe(CF₃)₂]₂ (**Mo** cat., 3.5 mg, 1.8 equiv) at room temperature and the reaction mixture was stirred for 2 h. To the reaction mixture was then added a dichloromethane (0.5 mL) solution containing tris(4-formylphenyl)amine [TPA(CHO)₃]

(corresponds to 0.3 mg/0.5 mL-CH₂Cl₂, 0.90 μmol, 1/3 equiv to PFV) and was stirred for 1 h. Into the reaction mixture, a toluene solution (1.0 mL) containing Mo(CHCMe₂Ph)(N-2,6-Me₂C₆H₃)-[OCMe(CF₃)₂]₂ (**Mo** cat., 5.8 mg, 3.0 equiv.) was added at room temperature, and the reaction mixture was stirred for 1 h for completion of reaction with the vinyl group. The reaction was then terminated by adding the prescribed aldehyde (Ar-CHO) in excess amount (10 equiv to the PFV) and was stirred for an additional 1 h for completion. The resultant star conjugated polymer was then precipitated by pouring in cold methanol and after stirring for two hours was then collected by filtration. The star polymer was then further purified as precipitate by using chloroform and methanol. The precipitates, collected by filtration were dried *in vacuo*, affording the star polymers, TPA[PFV-Ar]₃ as yellow-orange precipitates. Most of reactions were conducted with ca. 30 mg of PFV samples.

TPA[PFV-C₆F₅]₃. Yield 70-75 % (runs 1,8,9), or 52 % (run 2). ¹H NMR (CDCl₃ at 25 °C): δ 7.71 (br, Ar-H), 7.55 (br, Ar-H), 7.31 (br, *trans*-CH=CH-), 2.06 (br), 1.24-1.09 (m), 0.82 (t), 0.69 (br) ppm. In addition, small resonances at δ 7.21 (d, olefinic protons adjacent to TPA), and 7.16 (br, aromatic protons in TPA) ppm were observed.

TPA[PFV-C₆H₄NO₂]₃. Yield 39 %. ¹H NMR (CDCl₃ at 25 °C): δ 7.70 (br, 2H), 7.53 (br, 4H), 7.29 (br, 2H), 2.05 (br, 4H), 1.08 (br, 20H), 0.81 (m, 6H), 0.69 (br, 4H) ppm. In addition, small resonances at δ 7-8 ppm corresponding to resonances of aromatic protons etc. were observed.

TPA(PFV-DH4T)₃. Yield 46 %. ¹H NMR (CDCl₃ at 25 °C): δ 7.70 (br, 2H), 7.53 (br, 4H), 7.32 (br, 2H), 2.08 (br, 4H), 1.11 (br, 20H), 0.83 (m, 6H), 0.71 (br, 4H) ppm. In addition, small resonances at δ 7.00-8.00 (olefinic protons adjacent to TPA, aromatic protons in TPA), and 7.20-6.80 (m, 4T) ppm were observed.

TPA(PFV-3T)₃. Yield 47 %. ¹H NMR (CDCl₃ at 25 °C): δ: 7.69 (br, 2H), 7.54 (br, 4H), 7.30 (br, 4 H), 2.04 (br, 4H), 1.08 (m, 20H), 0.81 (m, 6H), 0.69 (br, 4H) ppm. In addition, small resonances at δ 7.00-8.00 (olefinic protons adjacent to TPA, aromatic protons in TPA), and 6.20-7.20 (m, 3T) ppm were observed.

TPTA(PFV-3T)₃. Yield 52 %. ¹H NMR (CDCl₃ at 25 °C): δ: 7.70 (br, 2H), 7.53 (br, 4H), 7.29 (br, 4 H), 2.04 (br, 4H), 1.09 (m, 20H), 0.80 (m, 6H), 0.69 (br, 4H) ppm. In addition, small resonances at δ 7.00-8.00 (olefinic protons adjacent to TPTA, aromatic protons in TPTA), and 6.20-7.20 (m, terthiophene) ppm were observed.

TPA(PFV-Fc)₃. Yield: 22-68%. ¹H NMR (CDCl₃ at 25 °C): δ 7.71 (d, Ar-H), 7.55 (br, Ar-H), 7.31 (br, *trans*-CH=CH-), 4.77-4.35 (ferrocenyl-H), 2.07 (br), 1.23-1.10 (m), 0.82 (t), 0.71 (br) ppm. In addition, small resonances at δ 7.21 (d, olefinic protons adjacent to TPA), 7.16 (br, aromatic protons in TPA), 6.87 and 6.60 (br, olefinic protons adjacent to Fc) were observed.

Synthesis of end-functionalized star block copolymers, TPA[₃(PFV)₂-3PV]-Ar or TPA[₃(PFV)₂-3T]-Ar

Into a stirred toluene solution (3.0 mL) containing a solution of poly(9,9-di-*n*-octyl-fluorene-2,7-vinylene) (PFV, 15 mg, 4.3 μmol, $M_{n(\text{calcd.})} = 3990$, $M_{n(\text{NMR.})} = 3500$) was added a toluene solution (1.0 mL) containing Mo(CHCMe₂Ph)(N-2,6-Me₂C₆H₃)[OCMe(CF₃)₂]₂ (**Mo** cat., 5.5 mg, 1.8 equiv) at room

temperature, and the reaction mixture was stirred for 2 h. Into the stirred mixture was then added 0.5 equiv of **3PVCHO** (3.5 mg, 2.1 μmol, in the case of runs 14, 15) or **3T(CHO)₂** (0.6 mg, 2.1 μmol, in the case of runs 16, 17) dissolved in dichloromethane (0.5 mL). The solution was then stirred for 1 h. The reaction mixture was then added a dichloromethane solution (0.5 mL) containing tris(4-formylphenyl)amine, [TPA(CHO)₃], (corresponds to 0.20 mg/0.5 mL-CH₂Cl₂, 0.72 μmol, 1/6 equiv to PFV), and was stirred for 1h. A toluene solution (1.0 mL) containing Mo(CHCMe₂Ph)(N-2,6-Me₂C₆H₃)-[OCMe(CF₃)₂]₂ (**Mo** cat., 9.2 mg, 3.0 equiv.) was then added to the reaction mixture at room temperature and the mixture was stirred for 1 h for completion of reaction with the vinyl group. Finally the reaction was terminated by adding the prescribed aldehyde (Ar-CHO) [Ar = C₆F₅ or Fc] in excess amount (10 equiv. to the PFV) and was stirred for an additional 1 h for completion.

The resultant star polymer was then precipitated by pouring in cold methanol and after stirring for two hours was then collected by filtration. The star polymer was then further purified as precipitate by using chloroform and methanol. The precipitates, collected by filtration were dried *in vacuo*, affording the star polymers as yellow-orange precipitates.

TPA[₃(PFV)₂-3PV]-C₆F₅]₃. Yield 69 %. ¹H NMR (CDCl₃ at 25 °C): δ 7.71 (br, Ar-H), 7.57-7.54 (br, Ar-H), 7.30 (br, *trans*-CH=CH-), 4.24-4.10 [-OCH₂CH₂OSi{CH(CH₃)₂]₃ of 3PV], 2.06 (br), 1.24-1.09 (m), 0.82 (t), 0.69 (br) ppm. In addition, small resonances at δ 7.22 (d, olefinic protons adjacent to TPA), 7.18 (br, aromatic protons in TPA) were observed.

TPA[₃(PFV)₂-3PV]-Fc]₃. Yield 40 %. ¹H NMR (CDCl₃ at 25 °C): δ 7.71 (d, Ar-H), 7.57-7.54 (br, Ar-H), 7.30 (br, *trans*-CH=CH-), 4.51-4.19 (ferrocenyl-H), 4.24-4.10 [-OCH₂CH₂OSi{CH(CH₃)₂]₃ of 3PV], 2.06 (br), 1.24-1.09 (m), 0.82 (t), 0.69 (br) ppm. In addition, small resonances at δ 7.18 (br, aromatic protons in TPA), 6.87 and 6.60 (br, olefinic protons adjacent to ferrocene) were observed.

TPA[₃(PFV)₂-3T]-C₆F₅]₃. Yield 93 %. ¹H NMR (CDCl₃ at 25 °C): δ 7.71 (br, Ar-H), 7.57-7.54 (br, Ar-H), 7.30 (br, *trans*-CH=CH-), 2.06 (br), 1.24-1.09 (m), 0.82 (t), 0.69 (br) ppm. In addition, very small resonances probably ascribed to olefinic protons adjacent to TPA, aromatic protons in TPA), and 6.20-7.20 (m, terthiophene) ppm were observed.

TPA[₃(PFV)₂-3T]-Fc]₃. Yield 67 %. ¹H NMR (CDCl₃ at 25 °C): 7.71 (br, Ar-H), 7.57-7.54 (br, Ar-H), 7.30 (br, *trans*-CH=CH-), 4.51-4.19 (ferrocenyl-H), 2.06 (br), 1.24-1.09 (m), 0.82 (t), 0.69 (br) ppm. In addition, small resonances at δ 7.21 (br, olefinic protons adjacent to TPA), 7.16 (br, aromatic protons in TPA), 7.05-7.00 (m, 3T), 6.93 and 6.81 (br, olefinic protons adjacent to Fc) were observed.

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Notes and references

^a Department of Chemistry, Faculty of Science and Engineering, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo 192-0397, Japan, Tel: +81-42-677-2547; E-mail: ktnomura@tmu.ac.jp

- ^b *Advanced Catalytic Transformation for Carbon Utilization (ACT-C)*, Japan Science and Technology Agency (JST), Saitama 332-0012, Japan
- † Electronic Supplementary Information (ESI) available: Experimental details for synthesis of starting polymer samples [poly(9,9-di-*n*-octyl-5-fluorene-2,7-vinylene)s (PFVs)], 2,4,6-Tris(4-formylphenyl)-1,3,5-triazine, selected NMR spectra and GPC traces for the end-functionalized star conjugated polymer samples. See DOI: 10.1039/b000000x/
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 - 20 Experimental details for synthesis and selected ¹H NMR spectra of polymers are shown in the Electronic Supplementary Information (ESI).
 - 21 The calibration with polystyrene standards often overestimates the molecular weight averages of rigid conjugated polymers. GPC curves vs structurally similar soluble PPP [poly(*p*-phenylene)] stds were thus recorded,^{12a} and the *M_n* values are overestimated by a factor of 1.6. Related article: D. Marsitzky, T. Brand, Y. Geerts, M., Klapper, K. Müllen, *Macromol. Rapid Commun.*, 1998, **19**, 385.
 - 22 The *M_n* values in the resultant polymers by method A are somewhat higher than those prepared by method B. This is because that the method A requires a purification step of “bis-alkylidene” species by

- washing with cold *n*-hexane for removal/separation of excess **Mo** catalyst and the *n*-hexane soluble fraction contains low molecular weight PFVs.
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- 24 Effect of charge transfer in Fe-bearing oligo/poly-thiophenes, (a) Y.
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- 25 Estimated number of each 9,9-di-*n*-octylfluorene-2,7-vinylene repeat
units are ca. 14 (run 11), 20 (run 8), 30 (runs 9 and 13) [$M_n(\text{calcd})$ of
starting PFV = 5760, 8370, 12400], respectively.
- 15 26 In reference 13b, we demonstrated that the unique fluorescence
spectra in PFV containing 3T at the chain ends (**PFV-3T**) would be
ascribed as due to an energy transfer from the PFV conjugated main
chain to the oligo(thiophene) moieties.
- 27 In reference 25c, attachment of Fe units to the poly(3-butylthiophene)
20 chain caused a dramatic quenching of photoluminescence in CH₂Cl₂
solution.
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Contents Abstract

Precise One-Pot Synthesis of Fully Conjugated End-Functionalized Star Polymers Containing Poly(fluorene-2,7-vinylene) (PFV) Arms**Kotohiro Nomura,***, Tahmina Haque, Tomohiro Miwata, Akiko Inagaki, Kenji Takamizu*Department of Chemistry, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo 192-0397, Japan; E-mail: ktnomura@tmu.ac.jp**Advanced Catalytic Transformation for Carbon Utilization (ACT-C), Japan Science and Technology Agency (JST), Saitama 332-0012, Japan*

A facile one-pot synthesis of end-functionalized star polymers consisting of PFVs has been achieved by olefin metathesis and Wittig-type coupling.

