Precise Synthesis of Poly(fluorene vinylene)s Capped with Chromophores: Efficient Fluorescent Polymers Modified by Conjugation Length and End-Groups

Kenji Takamizu,[†] Akiko Inagaki,[†] and Kotohiro Nomura*[,†,‡]

[†]Department of Chemistry, Faculty of Science and Engineering, Tokyo Metropolitan University, 1-1 minami Osawa, Hachioji, Tokyo 192-0397, Japan

[‡]Advanced Catalytic Transformation for Carbon Utilization (ACT-C), Japan Science and Technology Agency (JST), Saitama 332-0012, Japan

Ⓢ *Supporting Information*

ABSTRACT: Poly(9,9-di-*n*-octylfluorene-2,7-vinylene)s containing F-BODIPY [PFV-(F-BODIPY)$_2$] and Zn(II)-porphyrin have been prepared by olefin metathesis of the vinyl group in the PFV chain ends followed by subsequent Wittig-type coupling. An introduction of tris(2,5-dialkoxy-1,4-phenylene vinylene) into PFV-(F-BODIPY)$_2$ has also been achieved. The emission properties can be modified by the PFV chain length, chromophore, and the middle segment: PFV-(F-BODIPY)$_2$ exhibits white-light emission with high quantum efficiency.
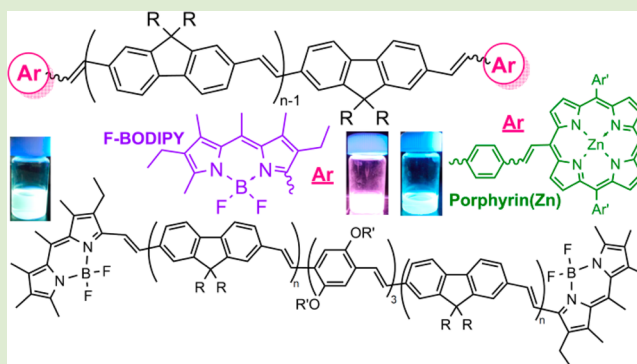
Organic electronics are important emerging technologies, and conjugated polymers/oligomers exemplified as poly(*p*-arylene vinylene)s are promising materials.[1−4] The importance of synthesis of structurally regular, chemically pure materials by new advanced synthetic methods/methodology has been recognized[1] for exhibition of notable device performances (affected by the structural regularity, chemical purity, and supramolecular order).[2,3] Precise synthesis of block copolymers has also been considered to be important in terms of their color modifications as well as formation of regular one-dimensional conjugated structures, and white polymer light-emitting diodes (WPLEDs,[5−7] especially single polymer systems consisting of a red component into a blue polymer chain[7]) are promising materials for their potential applications in full color flat panel displays etc.,[5] as well as for the great potential of flexibility and easy solution processing.[6] We recently demonstrated a precise synthesis of poly(9,9-dialkylfluorene-2,7-vinylene)s (PFVs) containing oligo(thiophene)s in both the chain ends, which exhibit unique emission properties by an energy transfer.[8]

We herein present efficient syntheses of PFVs containing chromophores at both chain ends and demonstrate that emission properties can be modified by introduction of the chromophores (end group functionality) as well as by the PFV chain length (conjugation repeat units). Through this communication, we wish to present that these polymers could be applied as highly efficient fluorescent polymers, especially white polymer light-emitting polymers with high efficiency.[9]

Poly(9,9-di-*n*-octylfluorene-2,7-vinylene)s (PFVs) prepared by the ADMET polymerization using a Ru catalyst[8,10] have been chosen because the resultant polymers not only possess well-defined chain ends as vinyl group, high molecular weights with uniform molecular weight distributions but also possess *defect-free* nature due to high stereoregularity (all-*trans*). An exclusive end functionalization can thus be achieved by treating the well-defined chain ends (vinyl groups) in PFVs[8,10] with Mo-alkylidene (Mo cat.) followed by Wittig-type cleavage with aldehyde.[8,10−13] PFVs with various M_n values (with uniform molecular weight distributions, shown in Table 1) were prepared by varying the reaction time (shown in the Supporting Information (SI)).[8,10a]

As shown in Scheme 1, vinyl groups in the PFVs' chain ends were treated with Mo(CHCMe$_2$Ph)(*N*-2,6-Me$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$ (**Mo** cat., 5 equiv) to afford the "bisalkylidene" species in situ,[8,10] and the subsequent addition of an excess amount of terephthalaldehyde afforded **PFV-(PhCHO)$_2$**.[14,15] The reaction of **PFV-(PhCHO)$_2$** with alkylidene species, that were prepared in situ by treatment of Zn(II)-5,15-di(4-*n*-butylphenyl)-10-vinylporphyrin with **Mo** cat., gave **PFV-[Porphyrin(Zn)]$_2$** in high yields [82−89% based on **PFV-(PhCHO)$_2$**].[15] Moreover,

Table 1. Selected Results for Syntheses of Poly(9,9-di-n-octylfluorene-2,7-vinylene)s (PFVs) Capped with Chromophores by Combined Olefin Metathesis with Wittig-Type Coupling[a]

PFV[b]			product		
M_n[c]	M_w/M_n[c]		M_n[c]	M_w/M_n[c]	yield[d]/%
3100 (4400)[e]	1.56 (1.46)[e]	PFV-[Porphyrin(Zn)]₂	6600	1.34	82.0
9400 (11500)[e]	1.83 (1.96)[e]	PFV-[Porphyrin(Zn)]₂	16500	1.86	87.4
9400 (11500)[e]	1.83 (1.96)[e]	PFV-[Porphyrin(Zn)]₂	15700	1.73	89.0
37000 (34000)[e]	1.80 (1.65)[e]	PFV-[Porphyrin(Zn)]₂	34700	1.38	82.5
8200	1.88	PFV-(F-BODIPY)₂	8400	1.82	91.5
18500	1.84	PFV-(F-BODIPY)₂	21100	1.58	95.7
18500	1.84	PFV-(F-BODIPY)₂	22000	1.75	94.7
28000	1.83	PFV-(F-BODIPY)₂	29500	1.83	>99.9
37000	1.80	PFV-(F-BODIPY)₂	39400	1.48	95.5
18500	1.84	3PV-(PFV-F-BODOPY)₂	39500	1.50	49.4

[a]Conditions: Experimental details, see Supporting Information.[15] [b]Starting PFV before modification. [c]GPC data in THF vs polystyrene standards. [d]Isolated yields. [e]M_n and M_w/M_n values (in brackets) for PFV-(PhCHO)₂.

Scheme 1. Synthesis of Poly(fluorene vinylene)s (PFVs) Capped with Chromophores[15]

the resultant in situ generated "bisalkylidene" species were treated with **F-BODIPY-CHO** (2,6-diethyl-5-formyl-1,7,8-trimethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene, BODIPY: boradiaza-indacene, boron-dipyrromethene)[16] that were prepared from **F-BODIPY** by oxidation with DDQ to afford **PFV-(F-BODIPY)₂** exclusively (>91.5% yields, Scheme 1), which were isolated simply by pouring the reaction mixture into methanol.[15,16] The M_n values in **PFV-[Porphyrin(Zn)]₂** and **PFV-(F-BODIPY)₂** were analogous to the estimated values

with uniform molecular weight distributions (M_w/M_n = 1.34−1.86, Table 1) without significant increases after these modification procedures. Moreover, resonances ascribed to protons of the vinyl groups in the starting PFVs were not observed in the ^{1}H NMR spectra, whereas resonances ascribed to protons in porphyrin moieties or F-BOPDIPY were clearly observed (with moderate integration ratios shown in the SI).[15] As described above, this is an established procedure for an exclusive introduction of oligo(thiophene)s[8] (and PEG unit[10a]
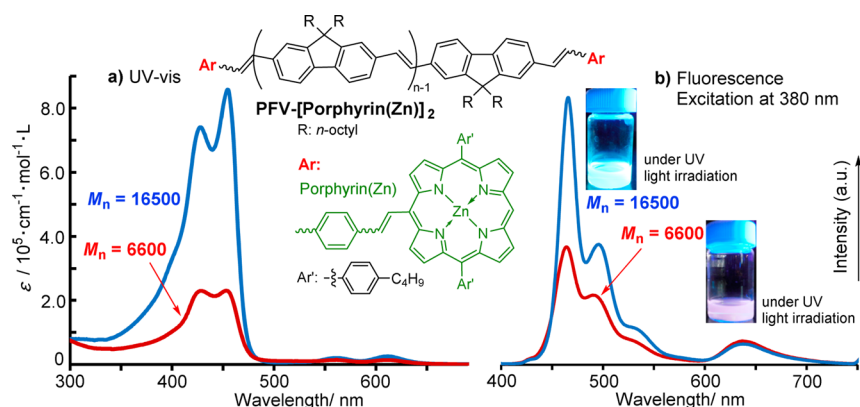
Figure 1. (a) UV−vis spectra (left) and (b) fluorescence spectra (right, excitation at 380 nm) for **PFV-[Porphyrin(Zn)]₂** in THF (conc. 1.0×10^{-6} M) at 25 °C.[17]

as well as initiating fragment for ATRP,[10b] etc.) into the PFV chain ends, and these results shown above strongly suggest that exclusive formations of **PFV-[Porphyrin(Zn)]₂** and **PFV-(F-BODIPY)₂** have been achieved by adopting this methodology.

Moreover, the resultant "bisalkylidene" species prepared in situ were treated with **3PV-CHO**[13] (0.5 equiv), and subsequent addition of **F-BODIPY-CHO** (excess amount) afforded triblock copolymers containing F-BODIPY moieties in both chain ends [Scheme 1, expressed as **3PV-(PFV-F-BODI-PY)₂**].[15] The M_n value was analogous to the estimated value with uniform molecular weight distribution ($M_w/M_n = 1.50$, Table 1), and protons ascribed to oligo(phenylene vinylene) and F-BODIPY were observed in the ¹H NMR spectrum.[15,17]

Figure 1 shows UV−vis and fluorescence spectra (in THF at 25 °C) for **PFV-[Porphyrin(Zn)]₂** with different molecular weights.[18] As reported previously,[19,20] the UV−vis spectra for PFV display two absorption bands at 455 and 427 (and 400) nm that can be ascribed to $\pi-\pi^*$ transitions (0−0, 0−1, and 0−2 transitions, respectively) of the conjugated backbone: the corresponding emission peaks at 465, 496, and 530 nm are observed in the fluorescence spectra.[19,20] Moreover, two absorption bands attributed to Zn(II)-porphyrin (two Q bands) are observed at 560 and 610 nm, which are shifted from the original (543 and 580 nm, Table 2). The absorbance at 430 nm was affected by the PFV conjugation length probably due to an energy transfer. Similarly, the relative intensity especially at 637 nm compared to the others (attributed to emissions to PFVs) in the fluorescence spectra increased upon decrease in the M_n value (PFV conjugation units): the relative intensities were also affected by the excitation wavelength (Figures S5 and S7, SI).[18] Note that the THF solutions containing **PFV-[Porphyrin(Zn)]₂** displayed amethyst-white (white-pale purple, $M_n = 6600$) or pale white-blue emission ($M_n = 16\,500$) under UV irradiation. The facts clearly suggest that blue light emission (by PFV) can be modified by an introduction of porphyrin (chromophore), and the emission color can also be tuned by the PFV conjugation units.

Figure 2 shows UV−vis and fluorescence spectra (in THF at 25 °C) for the resultant **PFV-(F-BODIPY)₂** with different molecular weights.[18] The absorption bands at 550 and 592 nm, which were shifted from that in the ordinary F-BODIPY analogues (519 nm, Table 2),[16,21] were observed in addition to three absorption bands attributed to PFV (at 455, 427, and 400 nm):[19,20] the relative absorbance in these bands was affected by the M_n value (PFV conjugation length). It seems likely that the observed large shift (550, 592 nm from 519 nm) in the UV−vis

Table 2. Summary of Optical Properties

product (M_n)[a]	absorption[b] λ_{max}/nm	fluorescence[c] λ_{max}/nm	Φ_{PL}[d]/%
PFV-[Porphyrin(Zn)]₂ (6600)	427, 451, 560, 610	465, 493, 531, 637	12
PFV-[Porphyrin(Zn)]₂ (16500)	426, 453, 560, 611	468, 495, 534, 637	17
PFV-(F-BODIPY)₂ (8400)	428, 451, 550, 592	468, 498, 537, 614	89
PFV-(F-BODIPY)₂ (29500)	428, 452, 547, 591	476, 497, 535, 613	89
3PV-(PFV-F-BODOPY)₂	428, 452	476, 497, 535, 613	69
PFV	427, 455	465, 496, 530	99[e]
Porphyrin(Zn)	410, 543, 580	590, 637	
F-BODIPY[f]	519	540	

[a]Details are shown in Table 1. [b]UV−vis spectra in THF (conc. 1.0×10^{-6} M) at 25 °C. [c]Fluorescence spectra in THF (conc. 1.0×10^{-6} M) at 25 °C, excitation wavelength at 460 m. [d]Photoluminescence quantum yield (Φ_{PL}) in THF (excitation wavelength at 460 nm) at 25 °C. [e]Cited from ref 20. [f]Spectra are shown in the SI.
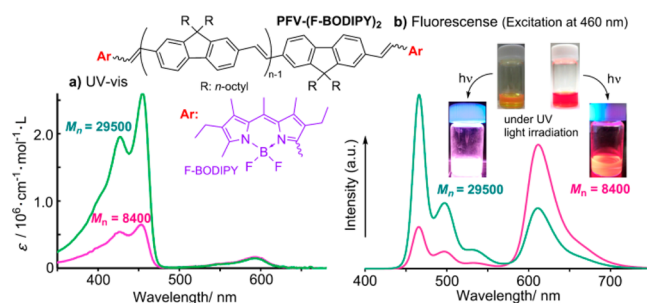

Figure 2. (a) UV−vis spectra (left) and (b) fluorescence spectra (right, excitation at 380 nm) for **PFV-(F-BODIPY)₂** in THF at 25 °C (conc. 1.0×10^{-6} M).[17]

spectrum would be due to an increase in the conjugation around F-BODIPY by connecting to PFV. A new broad emission band ($\lambda_{max} = 613-614$ nm) which is different from that in F-BODIPY itself[16,21] was observed in the fluorescence spectra: no significant differences in the intensities were observed even by varying the excitation wavelength (Figures S5 and S8, SI, excitation at 380 or 460 nm),[18] although the ratios in intensities of these λ_{max} values were influenced by the PFV conjugation length (M_n values, Figure 2 and Figure S6, SI).[18] The intensities of a broad emission band at 613−614 nm

were affected by the PFV conjugation length, probably due to influence of an energy transfer (from PFV to BODIPY under these excitation conditions). In contrast, significant differences were not observed in the fluorescence spectra of **PFV-(F-BODIPY)$_2$** with relatively high molecular weights (M_n = 22 000 and 29 500, Figure S6, SI).[18]

Note that the white-orange light emission of the THF solutions containing **PFV-(F-BODIPY)$_2$** (M_n = 8400) under UV irradiation can be tuned to *"white-light emission"* by varying the PFV conjugation units (M_n = 29 500). The facts clearly suggest that blue-light emission (by PFV) can be modified to the white-light emission by an introduction of functionality (F-BODIPY), and the emission property can also be tuned by varying the PFV conjugation units.[22] Moreover, as shown in Table 2, these *polymers displayed remarkably high photoluminescence quantum yields* (Φ_{PL} = 89%). The facts should be noteworthy because white-light-emitting diodes (WLEDs) have received considerable interest due to their potential applications,[5–7] as described in the introduction.

It should also be noted that the triblock copolymer, **3PV-(PFV-F-BODIPY)$_2$**, showed the white-light emission (Figure 3
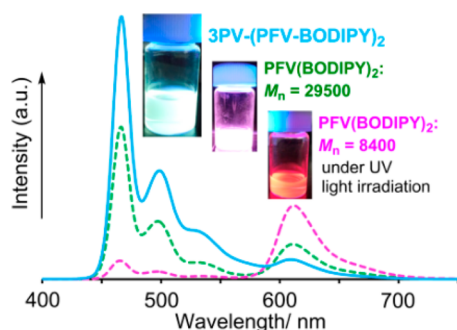

Figure 3. Fluorescence spectra (excitation at 460 nm) for **PFV-(BODIPY)$_2$** and **3PV-(PFV-F-BODOPY)$_2$** in THF at 25 °C (conc. 1.0×10^{-6} M).[17]

and Figures S9 and S10, SI), although the photoluminescence quantum yield (Φ_{PL} = 69%), the emission intensity (λ_{max} = 613–614 nm), and the absorbance at 550 and 592 nm decreased from **PFV-(F-BODIPY)$_2$**.[18] The fact thus suggests a possibility that the emission property can be modified by an introduction of the middle segment.

We have communicated that a precise, exclusive synthesis of conjugated polymers (PFVs) containing chromophores at the chain ends has been achieved by adopting olefin metathesis followed by Wittig-type coupling. In particular, white-light-emitting polymers with high quantum efficiency, **PFV-(F-BODIPY)$_2$** and **3PV-(PFV-F-BODIPY)$_2$**, have been prepared by adopting this methodology, and the emission properties can be tuned by introductions of the end groups, conjugation units, and middle segment. We highly believe that the present method should be highly promising for obtainment of polymers with the desired emission properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details for synthesis and identification of polymers and organic compounds, selected ^{1}H NMR spectra (in CDCl$_3$ at 25 °C), additional UV−vis and fluorescence spectra of the resultant polymers, and summary of CIEs. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: ktnomura@tmu.ac.jp.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) (a) Special Issue in Organic Electronics: *Chem. Mater.* **2004**, *16*, 4381. (b) *Organic Light Emitting Devices*; Müllen, K., Scherf, U., Eds.; Wiley-VCH: Winheim, 2006. (c) *Handbook of Conducting Polymers*, 3rd ed.; Skotheim, T. A., Reynolds, J., Eds.; CRC Press: Boca Raton, 2007.

(2) (a) Grimsdale, A. C.; Müllen, K. In *Macromolecular Engineering*; Matyjaszewski, K., Gnanou, Y., Leibler, L., Eds.; Wiley-VCH: Weinheim, 2007; Vol. 4, p 2225. (b) Bielawski, C. W.; Wilson, C. G. In *Macromolecular Engineering*; Matyjaszewski, K., Gnanou, Y., Leibler, L., Eds.; Wiley-VCH: Weinheim, 2007; Vol. 4, p 2263. (c) Laclerc, N.; Heiser, T.; Brochon, C.; Hadziioannou, G. In *Macromolecular Engineering*; Matyjaszewski, K., Gnanou, Y., Leibler, L., Eds.; Wiley-VCH: Weinheim, 2007; Vol. 4, p 2369.

(3) Selected reviews: (a) Fumitomo, H.; Díaz-García, M. A.; Schwartz, B. J.; Heeger, A. J. *Acc. Chem. Res.* **1997**, *30*, 430. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402. (c) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. C. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121. (d) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897. (e) Li, C.; Liu, M.; Pschirer, N. G.; Baumgarten, M.; Müllen, K. *Chem. Rev.* **2010**, *110*, 6817. (f) Zade, S. S.; Zamoshchik, N.; Bendikov, M. *Acc. Chem. Res.* **2011**, *44*, 14. (g) Zhou, H.; Yang, L.; You, W. *Macromolecules* **2012**, *45*, 607.

(4) (a) Stirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; de Leeuw, D. M. *Nature* **1999**, *401*, 685. (b) Hoofman, J. O. M.; de Haas, M. P.; Siebbeles, L. D. A.; Warman, J. M. *Nature* **1998**, *392*, 54. (c) Son, S.; Dodabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995**, *269*, 376.

(5) (a) D'Andrade, B. W.; Forrest, S. R. *Adv. Mater.* **2004**, *16*, 1585. (b) Kido, J.; Kimura, M.; Nagai, K. *Science* **1995**, *267*, 1332. (c) Wu, H.; Ying, L.; Yang, W.; Cao, Y. *Chem. Soc. Rev.* **2009**, *38*, 3391.

(6) For examples, see: (a) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477. (b) Zhang, Y.; Huang, F.; Chi, Y.; Jen, A. K. Y. *Adv. Mater.* **2008**, *20*, 1565. (c) Wu, H.; Zou, J.; Liu, F.; Wang, L.; Mikhailovsky, A.; Bazan, G. C.; Yang, W.; Cao, Y. *Adv. Mater.* **2008**, *20*, 696.

(7) For examples, see: (a) Lee, S. K.; Hwang, D. H.; Jung, B. J.; Cho, N. S.; Lee, J.; Lee, J. D.; Shim, H. K. *Adv. Funct. Mater.* **2005**, *15*, 1647. (b) Liu, J.; Zhou, Q.; Cheng, Y.; Geng, Y.; Wang, L.; Ma, D.; Jing, X.; Wang, F. *Adv. Mater.* **2005**, *17*, 2974. (c) Chuang, C.-Y.; Shih, P.-I.; Chien, C.-H.; Wu, F.-I.; Shu, C.-F. *Macromolecules* **2007**, *40*, 247. (d) Liu, J.; Cheng, Y.; Xie, Z.; Geng, Y.; Wang, L.; Jing, X.; Wang, F. *Adv. Mater.* **2008**, *20*, 1357. (e) Lin, Z.; Lin, Y.-D.; Wu, C.-Y.; Chow, P.-T.; Sun, C.-H.; Chow, T. J. *Macromolecules* **2010**, *43*, 5925.

(8) Kuwabara, S.; Yamamoto, N.; Sharma, P. M. V.; Takamizu, K.; Fujiki, M.; Geerts, Y.; Nomura, K. *Macromolecules* **2011**, *44*, 3705.

(9) The results were partly introduced at *International Kyoto Conference for Organic Chemistry* (November, 2012, Kyoto, Japan) and *10th IUPAC International Conference on Advanced Polymers via Macromolecular Engineering* (APME2013, August, 2013, Durham, UK).

(10) (a) Nomura, K.; Yamamoto, N.; Ito, R.; Fujiki, M.; Geerts, Y. *Macromolecules* **2008**, *41*, 4245. (b) Abdellatif, M. M.; Nomura, K. *ACS Macro Lett.* **2012**, *1*, 423.

(11) For selected reviews for ADMET polymerization, see: (a) Lehman, S. E., Jr.; Wagener, K. B. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; *Vol. 3*, p 283. (b) Baughman, T. W.; Wagener, K. B. In *Metathesis Polymerization*; Buchmeiser, M. R., Ed.; Springer: Heidelberg, 2005; p 1. (c) Berda, E. B.; Wagener, K. B. In *Polymer Science: A Comprehensive Reference*; Matyjaszewski, K., Müllen, M., Eds.; Elsevier BV: Amsterdam, 2012; *Vol. 5*, p 195. (d) Berda, E. B.; Wagener, K. B. In *Synthesis of Polymers; New Structures and Methods*; Schluter, D., Hawker, C., Sakamosto, J., Eds.; Wiley-VCH: Weinhein, Germany, 2012; p 587. (e) Atallah, P.; Wagener, K. B.; Schulz, M. D. *Macromolecules* **2013**, *46*, 4735.

(12) (a) Nomura, K.; Takahashi, S.; Imanishi, Y. *Macromolecules* **2001**, *34*, 4712. (b) Murphy, J. J.; Kawasaki, T.; Fujiki, M.; Nomura, K. *Macromolecules* **2005**, *38*, 1075. (c) Murphy, J. J.; Furusho, H.; Paton, R. M.; Nomura, K. *Chem.—Eur. J.* **2007**, *13*, 8985. (d) Nomura, K.; Abdellatif, M. M. *Polymer* **2010**, *51*, 1861.

(13) Synthesis of end-functionalized oligo(2,5-dialkoxy-1,4-phenylene vinylene)s by combined olefin metathesis and Wittig coupling: Abdellatif, M. M.; Nomura, K. *Org. Lett.* **2013**, *15*, 1618.

(14) Synthetic procedures for Zn(II)-5,15-di(4-*n*-butylphenyl)-10-vinyl-porphyrin and **PFV-(PhCHO)₂** including their identifications are shown in the Supporting Information. Synthesis of 10-bromo-5,15-di(4-*n*-butylphenyl)porphyrin was performed by the analogous procedure for reported synthesis of 10-bromo-5,15-di-*p*-tolyl-porphyrin: Takanami, T.; Hayashi, M.; Chijimatsu, H.; Inoue, W.; Suda, K. *Org. Lett.* **2005**, *7*, 3937.

(15) Syntheses of **PFV-[Porphyrin(Zn)]₂**, **PFV-(F-BODIPY)₂**, and **PV-(PFV-F-BODIPY)₂** including their identifications are shown in the Supporting Information.

(16) Detailed synthetic procedures including their identifications are shown in the Supporting Information. (a) F-BODIPY (8-methyl) was prepared by an analogous method for synthesis of the 8-decyl analogue: Nagai, A.; Miyake, J.; Kokado, K.; Nagata, Y.; Chujo, Y. *J. Am. Chem. Soc.* **2008**, *130*, 15276. (b) Oxidation of 8-iodophenyl analogue by DDQ, see: Haefele, A.; Zedde, C.; Retailleau, P.; Ulrich, G.; Ziessel, R. *Org. Lett.* **2010**, *12*, 1627.

(17) For synthesis of **3PV-(PFV-F-BODOPY)₂**], "bisalkylidene" species, prepared by reaction of the vinyl groups in PFV with Mo catalyst (5 equiv), were isolated by washing with *n*-hexane because the Mo catalyst is highly soluble in *n*-hexane. Then, 0.5 equiv of 3PV-CHO (in toluene) was added into the toluene solution containing the "bisalkylidene" species. The method can provide efficient synthesis of various end-functionalized block copolymers. The results were partly introduced at *20th International Symposium on Olefin Metathesis and Related Chemistry* (ISOMXX, P18, July, 2013, Nara, Japan). Estimation of the M_n values, $M_{n(calcd)} = 25\,300$ [on the basis of $M_{n(GPC)}$: corrected value]; $M_{n(NMR)} = 23\,400$ (integration ratio), and the data shown in the SI.

(18) Additional UV−vis and fluorescence spectra of the resultant polymers are shown in the SI.

(19) (a) Anuragudom, P.; Newaz, S. S.; Phanichphant, S.; Lee, T. R. *Macromolecules* **2006**, *39*, 3494. (b) Liu, Q.; Liu, W.; Yao, B.; Tian, H.; Xie, Z.; Geng, Y.; Wang, F. *Macromolecules* **2007**, *40*, 1851.

(20) Yamamoto, N.; Ito, R.; Geerts, Y.; Nomura, K. *Macromolecules* **2009**, *42*, 5104.

(21) Yeo, H.; Tanaka, K.; Chujo, Y. *Macromolecules* **2013**, *46*, 2599.

(22) CIE values (under excitation of 460 nm) of **PFV-[Porphyrin(Zn)]₂**, **PFV-(F-BODIPY)₂**, and **PV-(PFV-F-BODIPY)₂** are shown in the SI. These values were somewhat different from those expected in the samples with white-light emission, but the results clearly indicate that these values can be modified by the PFV conjugation length, end group, and middle segment. It thus seems

likely that the observed white light would be a consequence of emissions under UV light irradiation (mixture of several excitation wavelengths).