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Precise Synthesis of End-Functionalized Oligo(2,5-dialkoxy-1,4-phenylene vinylene)s with Controlled Repeat Units via Combined Olefin Metathesis and Wittig-Type Coupling

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ABSTRACT

The precise synthesis of chemically, analytically pure oligo(2,5-dialkoxy-1,4-phenylene vinylene)s [OPVs, alkoxy = $O(CH_2)_2OSi^iPr_3$] with strictly controlled repeat units (up to 15 repeat units) and well-defined end groups has been achieved by a combined olefin metathesis reaction of 2,5-dialkoxy-1,4-divinylbenzene or their derivatives with a molybdenum–alkylidene complex and the subsequent Wittig-type cleavage with their dicarboxaldehyde analogues. The effects of the repeat units and the end functional groups toward their UV–vis and the fluorescence spectra have been clearly demonstrated.

Organic electronics have been recognized as important emerging technologies, and conjugated polymers/oligomers exemplified as poly(*p*-arylene vinylene)s are promising semiconducting materials.[1–4] The synthesis of structurally regular, chemically pure materials by development of new synthetic methods/methodology has attracted considerable attention[1] because their device performances are affected by their structural regularity, chemical purity, and supramolecular order.[2,3] We recently demonstrated syntheses of defect-free, stereoregular (all-*trans*), high molecular weight poly(9,9-dialkylfluorene-2,7-vinylene)s (PFVs),[5] poly(2,5-dialkylphenylene-1,4-vinylene)s (PPVs),[6] etc. by acyclic diene metathesis (ADMET) polymerization.[5–11] Since the resultant polymers prepared by a Ru-carbene catalyst

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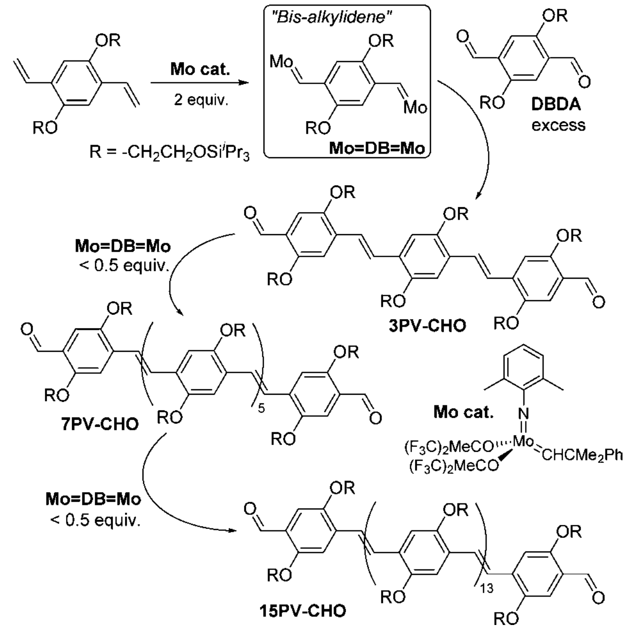
possessed well-defined chain ends (as vinyl group),[5b−e,6] an exclusive end-functionalization can be achieved by treating the vinyl groups with Mo-alkylidene (**Mo** cat.) followed by Wittig-type cleavage with aldehyde.[5b,d,e,12,13] We thus demonstrated precise syntheses of amphiphilic (multi)block copolymers,[5b,e] and of PFV's containing oligo(thiophene)s in both chain ends which exhibit unique emission properties by an energy transfer.[5d]

Synthesis of oligo(2,5-dialkoxy-1,4-phenylene vinylene)s (OPVs) by the ADMET technique was reported;[9] however, oligomers up to 7 (average 3) repeat units were prepared,[9b] and synthesis of high molecular weight oligomers seemed difficult due to coordination of an O-atom toward the centered metal (Mo, Ru, etc.) and/or accompanied catalyst decomposition.[9g] Since the above Wittig-type reactions of Mo-alkylidene species with aldehydes took place in quantitative yields,[5b,d,e] here, we thus wish to present a precise, exclusive synthesis of analytically pure OPVs with strictly controlled repeat units and well-defined chain ends, achieved by (repetitive stepwise) coupling of the "bis-alkylidene" species with OPV containing aldehyde at the both chain ends (Scheme 1).[14,15]

Scheme 1. Synthesis of Analytically Pure OPVs



We have thus chosen a stepwise approach for synthesis of conjugated oligomers (Scheme 1). The vinyl groups in **DVB** were treated with Mo(CHCMe$_2$Ph)(N-2,6-Me$_2$C$_6$H$_3$)-[OCCH$_3$(CF$_3$)$_2$]$_2$, (**Mo** cat., 2 equiv), to form the "bis-alkylidene" species (expressed as **Mo=DB=Mo**) *in situ*, and subsequent reaction with corresponding aldehyde (2,5-dialkoxybenzene-1,4-dicarboxaldehyde, **DBDA**) in a rather excess amount (2.2 equiv to **DVB**) afforded a 3-mer containing aldehyde as the end groups (expressed as **3PV-CHO**). **3PV-CHO** was isolated as an analytically pure form by a simple fractional separation (yield 85.0%) and

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(15) Detailed experimental procedures including syntheses and identifications of all oligo(2,5-dialkoxy-phenylene vinylene)s presented in this paper, selected NMR spectra, GPC traces are shown in the Supporting Information (SI). An attempted synthesis of high molecular weight polymers by ADMET polymerization of 2,5-bis(2′-triisopropylsilyloxyethoxy)-1,4-divinylbenzene (**DVB**) using a Ru-carbene catalyst, RuCl$_2$(PCy$_3$)(IMesH$_2$)(CH-2-O^{i}Pr-C$_6$H$_4$) [Cy = cyclohexyl, IMesH$_2$ = 1,3-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene], was not successful [$M_{n(GPC)} = 2.9 \times 10^3$, $M_{n(NMR)} = 1.87 \times 10^3$, $M_w/M_n = 1.27$]. The result is also shown in the SI.

was identified by NMR spectra, GPC trace (unimodal distribution, M_w/M_n = 1.0), and elemental analysis.[15] The M_n value estimated by the ^{1}H NMR spectrum (on the basis of integration ratio of aromatic protons in OPV vs chain end group) was very close to the calculated value (Table 1).

Moreover, **3PV-CHO** was treated with < 0.5 equiv of the "bis-alkylidene" species to afford the 7-mer (**7PV-CHO**) as the sole coupled product.[15] Then, the resultant **7PV-CHO** was treated with < 0.5 equiv of the "bis-alkylidene" species to afford the 15-mer (**15PV-CHO**) exclusively.[15] **7PV-CHO** was isolated as an analytically pure form by a fractional separation (isolated yield 80.0%) and identified by NMR spectra, GPC trace (M_w/M_n = 1.0), and elemental analysis:[15] **15PV-CHO** was also isolated as a pure form confirmed by fractional GPC (in addition to ordinary GPC traces, M_w/M_n = 1.0) and identified by NMR spectra (isolated yield 82.0%). The M_n values in **7PV-CHO** and **15PV-CHO** estimated by ^{1}H NMR spectra were very close to the calculated values. Note that a synthesis of high molecular weight oligomers [ex. **15PV-CHO**, M_n = 8.07 × 10^3] has been achieved by adopting this methodology and that the resultant oligomer possessed strictly repeat units with well-defined end groups. Moreover, it should also be noted that the olefinic double bond in the OPVs possessed high stereoregularity (highly *trans*) confirmed by ^{1}H NMR spectra.[15]

Table 1. Synthesis of OPVs with Well-Defined End Functional Groups [alkoxy (OR) = $O(CH_2)_2OSi^iPr_3$]^a

OPVs	$M_{n(NMR)}$^{b} ×10^{-3}	$M_{n(calcd)}$^{c} ×10^{-3}	M_w/ M_n^{d}	yield^e/ %	absorption^f λ_{max}/nm	fluorescence^g λ_{max}/nm
3PV-CHO	1.63	1.63	1.0	85.0	276,432	540
7PV-CHO	3.76	3.78	1.0	80.0	459	532
15PV-CHO	8.04	8.07	1.0	82.0	476	539
5PV-3T	3.24	3.29	1.0	85.0	463	527
5PV-C_6H_5	2.84	2.84	1.0	85.0	470	535
5PV-C_6F_5	3.02^h	3.03	1.0	95.0	450	531

^{a}Conditions: Experimental details are shown in the Supporting Information.[15] ^{b}Estimated by ^{1}H NMR spectra (on the basis of integration ratios of aromatic protons in **OPV** vs chain end group). ^{c}Calculated on the basis of formula, molar ratios. ^{d}GPC data in THF vs polystyrene standards. ^{e}Isolated yield. ^{f}On the basis of UV−vis spectra (in THF at 25 °C). ^{g}On the basis of fluorescence spectra (in THF at 25 °C). ^{h}M_n value estimated on the basis of methylene protons in the alkoxy group vs aromatic protons.

Importantly, **3PV-CHO** was reacted with ca. 2.2 equiv of the "bis-alkylidene" species, and subsequent addition of 2,2′:5′,2″-terthiophene-5-carboxaldehyde (3T-CHO) afforded the 5-mer of the oligo(2,5-dialkoxy-1,4-phenylene vinylene) containing an oligo(thiophene) moiety at both chain ends (expressed as **5PV-3T**, Scheme 2). Similarly, the reaction with C_6F_5CHO, PhCHO in place of 3T-CHO afforded the 5-mer containing C_6F_5 or C_6H_5 end groups (**5PV-C_6F_5**, **5PV-C_6H_5**, respectively). The resultant oligomers (**5PV-3T**, **5PV-C_6F_5**, **5PV-C_6H_5**) were also isolated as analytically pure forms by a simple fractional separation and were identified by NMR spectra, GPC trace (M_w/M_n = 1.0), and elemental analysis.[15] The M_n values estimated by ^{1}H NMR spectra in these 5PVs were very close to the calculated values (Table 1). These results clearly indicate that a precise synthesis of analytically pure oligomers that possess strictly repeat units and various well-defined end groups has been achieved by adopting this approach.

Scheme 2. Synthesis of OPVs with Well-Defined End Groups

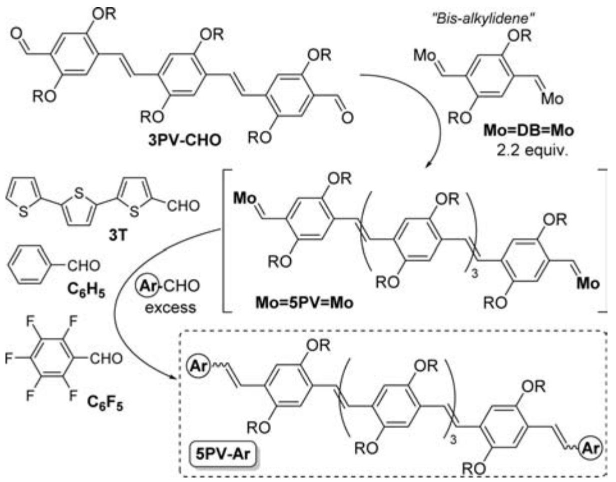

Figure 1 shows UV−vis (left) and fluorescence (right, excitation wavelength at 450 nm) spectra (in THF, 1.0 × 10^{-6} M at 25 °C) for the resultant OPVs (**3PV-CHO**, **7PV-CHO**, **15PV-CHO**) and starting divinylbenzene (**DVB**). Different absorption bands observed were due to the influence of the conjugation repeat units: the λ_{max} values, which have been known to be attributed to the $\pi-\pi^*$ transition of the conjugated backbone,[9e,16] shifted to a longer wavelength (the maximum of the $S_1 \leftarrow S_0$ electronic transition shifts toward lower energies) upon the increase in the conjugation units [λ_{max}: 276 and 432 nm (**3PV-CHO**), 459 nm (**7PV-CHO**), 476 nm (**15PV-CHO**)]. In contrast to the absorption, as reported previously,[9e,16] the recorded fluorescence spectra showed a vibronic splitting where the relative intensity of the $S_1 \rightarrow S_0$ 0−0 compared to the 0−1 electronic transition seems to increase upon increasing conjugation length [λ_{max}: 540 nm (**3PV-CHO**), 532 nm (**7PV-CHO**), 539 nm (**15PV-CHO**)]. Moreover, photoluminescence quantum yields in the resultant **3PV-CHO**, **7PV-CHO**, and **15PV-CHO** (in THF at 25 °C, excitation at 450 nm) were 0.83, 0.62, and 0.51, respectively. These values

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(17) (a) Effect of conjugation length toward the photoluminescence quantum yields in α,ω-dimethyl-oligo{2,5-bis[2-(*S*)-methylbutoxy]-*p*-phenylene vinylenes: Peeters, E.; Ramos, A. M.; Meskers, S. C. J.; Janssen, R. A. *J. Chem. Phys.* **2000**, *112*, 9445. The yields (in $CHCl_3$) were 0.62 (OPV3, trimer), 0.49 (OPV5, pentamer), and 0.25 (OPV7, heptamer), respectively. (b) The value (0.51 in **15PV-CHO**) was also higher than that reported (0.35) in poly(2-methoxy-5-(2′-ethylhexoxy)-1,4-phenylene vinylene). Samuel, I. D. W.; Rumbles, G.; Friend, R. H. In *Primary Photoexcitations in Conjugated Polymers*; Sariciftci, N. S., Ed.; World Scientific: Singapore, 1997; Chapter 7, p 140.

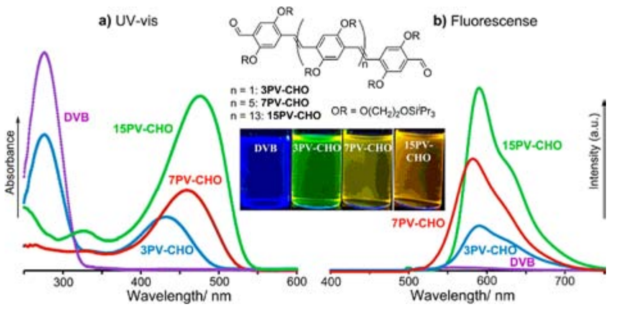

Figure 1. UV–vis spectra (left) and the fluorescent spectra (right, excitation at 450 nm) for **DVB**, **3PV-CHO**, **7PV-CHO**, and **15PV-CHO** in THF at 25 °C (concn 1.0 × 10^{-6} M).

were somewhat higher than those for reported OPVs with different side and end groups:[17] significant decreases in the values were not observed even with **15PV-CHO**, which would be an interesting contrast to those reported previously.[17]

Figure 2 shows UV–vis (left) and fluorescence (right, excitation wavelength at 450 nm) spectra (in THF, 1.0 × 10^{-6} M at 25 °C) for the **5PVs** with different end functional groups (**5PV-3T**, **5PV-C_6F_5**, **5PV-C_6H_5**). The λ_{max} values in the UV–vis spectra were varied by the introduction of end functional groups [λ_{max}: 463 nm (**5PV-3T**), 450 nm (**5PV-C_6F_5**), 470 nm (**5PV-C_6H_5**)], which would be assumed, as the charge transfer band is shifted by an increase of the electron-withdrawing power of the acceptor.[18] Moreover, the fluorescence intensities were affected by the end functional group probably due to a degree of energy transfer, suggesting that the emission properties can be modified by the introduction of an end functional group.

We have shown that a precise, exclusive synthesis of oligo(2,5-dialkoxy-1,4-phenylene vinylene)s [OPVs, up to 15 repeat units, alkoxy (OR) = O(CH$_2$)$_2$OSi^{i}Pr$_3$] with strictly controlled repeat units and well-defined end functional groups has been achieved by adopting a stepwise coupling of the "bis-alkylidene" species with OPVs containing an aldehyde at both chain ends (Schemes 1, 2). Moreover, the resultant oligomers are structurally regular (highly *trans* olefinic double bonds) and chemically pure and were identified by NMR spectra and elemental analysis. The optical properties (in their UV–vis and fluorescence spectra) can be modified by both the conjugation repeat units and the end functional groups.

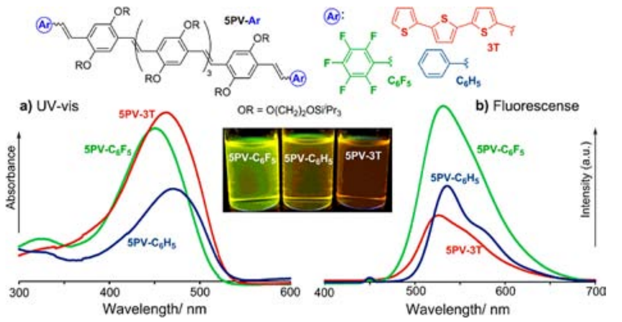

Figure 2. (a) UV–vis spectra (left) and (b) fluorescent spectra (right, excitation at 450 nm) for **5PV-Ar** (Ar = 3T, C_6F_5, C_6H_5) in THF at 25 °C (concn 1.0 × 10^{-6} M).

The methodology presented here is, as far as we know, the rare demonstration of a precise synthesis of end-functionalized oligo(arylene vinylene)s, and a wide applicability of this methodology enables us to fine-tune various conjugated oligomers/polymers with unique properties. We highly believe that the methodology presented here should be thus highly promising for designing precise conjugated materials for the desired purposes. More details, including the effect of various conjugation lengths and end functional groups toward basic optical properties are now in progress.

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Supporting Information Available. Experimental procedures for syntheses of monomers and oligomers including their identification. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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(18) It seems likely from Figure 2 (right) that the relative intensity ascribed to the $S_1 \rightarrow S_0$ 0–0 and the 0–1 electronic transition were affected by the end functional groups.[5d] The report for tunable optical properties of chromophores in OPV (up to 3 mer): Guerlin, A.; Dumur, F.; Dumas, E.; Miomandre, F.; Wantz, G.; Mayer, C. R. *Org. Lett.* **2010**, *12*, 2382.