Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron Letters 47 (2006) 2731–2734

Tetrahedron Letters

Oligo(phenylene vinylene)–poly(methylstyrene) hybrids: controlled step-wise molecular wiring of oligo(phenylene vinylene)

Rethi Madathil,* Raman Parkesh† and Sylvia M. Draper

Science Foundation Ireland, Physics Department and Chemistry Department, Trinity College, Ireland

Received 15 September 2005; revised 9 February 2006; accepted 15 February 2006
Available online 3 March 2006

Abstract—Well defined oligo(phenylene vinylene) grafted polymers known as oligo(phenylene vinylene)–poly(methylstyrene) hybrids have been developed using a step-wise synthetic protocol, where the length of the OPV can be controlled systematically to achieve specific optoelectronic properties. The process allows the structural modification of attached OPV at a molecular level either by varying the chain length or by changing functionalities. The step-wise generation of OPV chains on the backbone of a highly soluble polymer ensures solubilization in a variety of solvents and also the exhibition of interesting optical properties.

The organic semiconducting materials, poly(phenylene vinylene) and oligo(phenylene vinylene) (OPV), have attracted intense research interest because of their attractive electroluminescent properties.[1] The realization of optoelectronic devices with OPV as the active layer, requires the design of new structures with specific optoelectronic features. Great success has been achieved in developing OPV based supramolecular structures such as dendrimers[2] tetrahedral OPVs[3] and self-assembled structures.[4]

From an applications point of view, mechanical flexibility is highly desired to obtain deposition as a thin film over a large area. Successful physical blending depends on the compatibilty of the components, where the intractable nature of OPVs is disadvantageous. Only soluble alkoxy substituted OPVs are considered as suitable candidates for blending.[5] New strategies that result in high quality blends of OPVs with flexible inert polymers are therefore technologically important. Recently developed copolymers of OPV with non-conjugated polymers are promising due to their higher processability.[6–11] However, OPVs with greater chain length are insoluble and hence difficult to incorporate directly into processable polymers. Consequently, OPV-copolymers so far designed have chain lengths of the OPV unit limited to a maximum of three.[6–11] In this context a strategy that integrates long chain OPV oligomers on flexible polymers is interesting.

The present work explores the step-wise wiring of OPV into higher oligomers on mechanically flexible poly(methylstyrene). The development of OPV chains via step-wise addition of a stilbenoid unit on a highly soluble polymer ensures solubilization in a variety of solvents. The proposed method gives a choice of growing unmodified OPV or other substituted forms. The high solubility of the polymer hybrids at each step permits the further attachment of stilbenoid units.

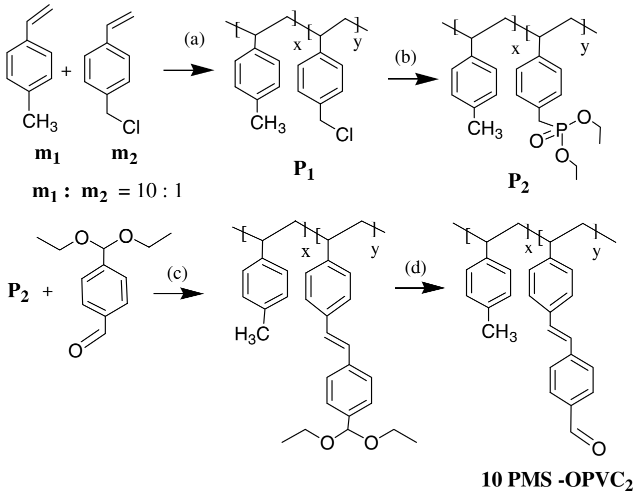
We selected poly(methylstyrene) as the inert polymer backbone to undergo OPV wiring. The precursor polymer poly(4-methylstyrene-co-4-chloromethylstyrene), $\mathbf{P_1}$ consisting of 10 equiv of 4-methylstyrene and 1 equiv of 4-chloromethylstyrene was synthesized using benzoyl peroxide as the polymerization initiator[12] (Scheme 1). The high content of methylstyrene in the precursor polymer induces solubility. The chloromethyl functionalities on $\mathbf{P_1}$ were then converted to phosphonates[13] by treatment with a large excess of triethylphosphite at 140 °C to give $\mathbf{P_2}$ (Scheme 1). The $\mathbf{P_2}$ polymers were subsequently subjected to a Wittig–Horner reaction[14] with 4-(diethoxymethyl)benzaldehyde followed by treatment with 1 M HCl to obtain the first generation polymer, **10PMS-OPVC$_2$**. Monomer $\mathbf{m_3}$, necessary for further attachment of OPV was prepared as illustrated in Scheme 2. We have established a simple protocol for the synthesis of $\mathbf{m_3}$ in bulk quantities.[15]

Keywords: Hybrid polymer; Step-wise wiring; Optoelectronic properties.

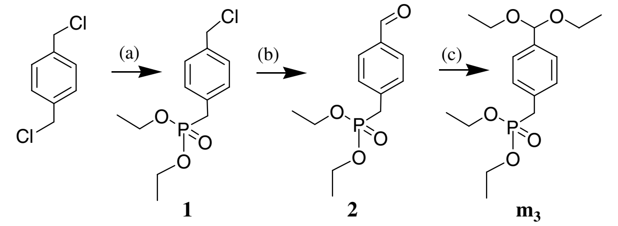
* Corresponding author. E-mail: madathir@tcd.ie

† Present address: Pharmacology Department, University of Oxford, Oxford, UK.

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.02.088



Scheme 1. Synthesis of **10PMS-OPVC$_2$**. Reagents and conditions: (a) benzoyl peroxide, 130 °C, 6 h, (b) triethylphosphite, 140 °C, 24 h, (c) potassium-*tert*-butoxide, THF, rt, 24 h, (d) 1 M HCl, 3–5 min.

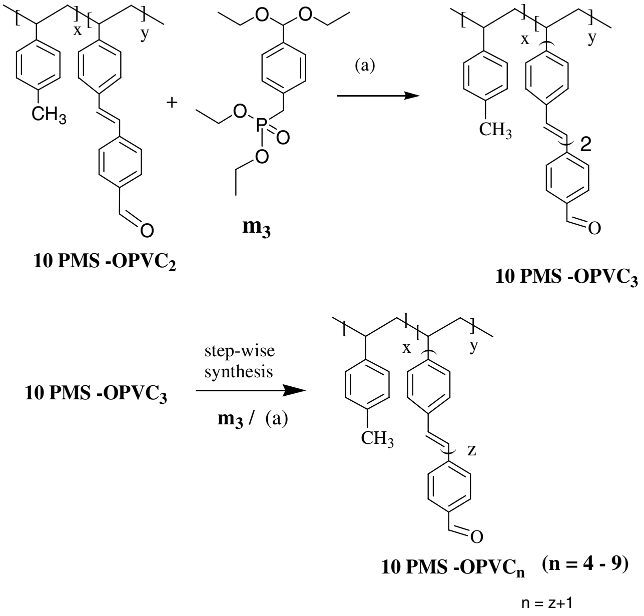


Scheme 2. Synthesis of monomer **m$_3$**. Reagents and conditions: (a) triethylphosphite, 120 °C, 3 h, (b) hexamethylene tetraamine, acetic acid, 100 °C, 3 h and then concd HCl, 100 °C, 15 min, (c) triethyl orthoformate, *N*-bromosuccinimide, ethanol, rt, 12 h.

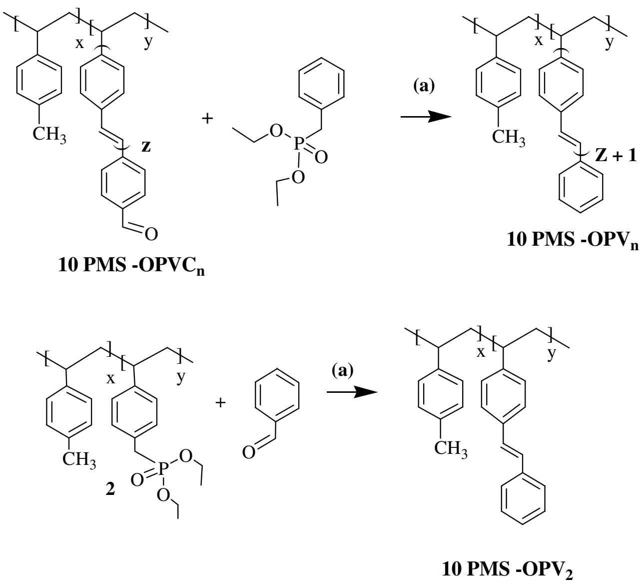
Aldehyde functionalized **10PMS-OPVC$_2$** was systematically subjected to Wittig reaction with monomer **m$_3$**, in a step-wise manner to attach stilbenoid units as shown in Scheme 3. To ensure the complete transformation of OPV at each stage to the next higher oligomer, a large excess of monomer **m$_3$** was used. The polymers obtained were semi-crystalline, bright yellow powders.

These aldehyde functionalized **10PMS-OPVC$_n$** polymers were then reacted with 4-diethylbenzylphosphonate to obtain phenylene end-functionalised **10PMS-OPV$_n$** (Scheme 4). Hybrid polymer **10PMS-OPV$_2$** was synthesized by treating **P$_2$** with benzaldehyde. All the polymers were highly soluble in a variety of solvents such as THF, ethyl acetate, dichloromethane and toluene. The absorption and fluorescence spectra of polymers **10PMS-OPVC$_n$** are depicted in Figure 1.

The absorbance maxima are red-shifted with increased chain length. The polymers, where *n* is 2 and 3–4 exhibited absorption maxima at 337 nm and ~360 nm, respectively, indicating a decrease in the energy of absorption with increase in chain length. Hybrid polymers **10PMS-OPVC$_{5–9}$** exhibit absorption features comparable to each other with maxima between 370 and 380 nm. **10PMS-OPVC$_2$** showed blue coloured emission at 440 nm.



Scheme 3. Step-wise synthesis of **10PMS-OPVC$_n$** polymer hybrids with chain length $n = 4–9$. Reagents and conditions: (a) potassium-*tert*-butoxide, THF, rt, 24 h and then 1 M HCl, 3–5 min.



Scheme 4. Synthesis of **10PMS-OPV$_n$** polymer hybrids. Reagents and conditions: (a) potassium-*tert*-butoxide, THF, rt, 24 h.

Polymers **10PMS-OPVC$_{3–9}$** showed only a slight change in fluorescent emission characteristics as depicted in Figure 1. (**10PMS-OPVC$_2$** at 462 nm, **10PMS-OPVC$_3$** at 467 and **10PMS-OPVC$_{4–9}$** at 472–478 nm) with intense emission in the blue-green region. The electron withdrawing nature of the aldehyde group in these polymers enhances delocalization of electrons in a similar fashion in all these polymers, resulting in broad absorption bands.

Absorption spectra of phenylene end-functionalised **10PMS-OPV$_n$** polymers show significant changes in

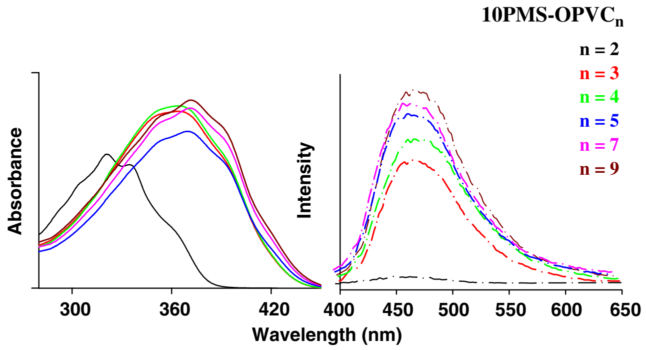


Figure 1. UV–vis absorption and fluorescence spectra (λ_{exc} 337 nm for $n = 2$, 360 nm for $n = 3$ and 373–380 nm for $n = 4$–9 for **10PMS-COPV$_n$** polymers in THF solution).

the spectral characteristics with chain length as illustrated in Figure 2. As the chain length increases, a significant shift in absorption towards low energy is observed (absorption maxima for **10PMS-OPV$_2$** at 300 nm, for $n = 3$–4, 330–335 nm and for $n = 5$–9 between 370 and 380 nm) indicating the increase in effective conjugation length. Absorption spectra were similar to the corresponding OPV oligomers.[14]

The fluorescent spectra of **10PMS-OPV$_n$** were highly structured with defined fluorescent bands, compared to the broad spectra of **10PMS-OPVC$_n$** polymer hybrids. The spectral bands were shifted to the lower energy with increase in conjugation length (**10PMS-OPV$_2$** at 358 nm, 397–420 nm for $n = 3$, 460 nm for $n = 4$, for $n = 5$–9 between 460 and 480 nm). As the chain length increases the emission colour changes from violet to green (Fig. 2).

In summary, this work explores a step-wise synthetic strategy to obtain oligo(phenylene vinylene)–poly(methylstyrene) hybrids where the length of the OPV can be controlled systematically to achieve specific optoelectronic properties. The protocol allows the structural modification of attached OPV at a molecular level either by varying the chain length or by changing the functionalities.

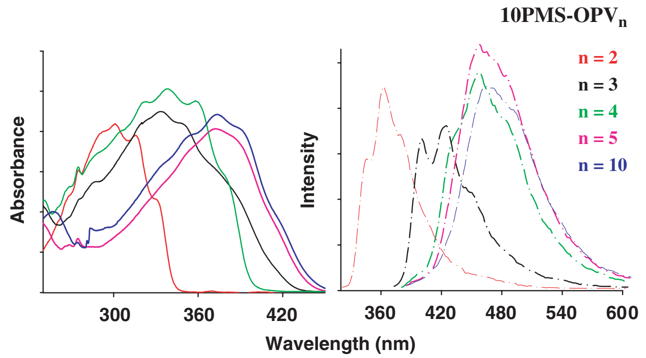


Figure 2. UV–vis absorption and fluorescence spectra (λ_{exc} 300 nm for $n = 2$, 330 nm for $n = 3$–4 and 365 nm for $n = 5$–9 for **10PMS-OPV$_n$** polymers in THF solution).

Acknowledgements

Dr. R. Madathil acknowledges the Science Foundation Ireland (CINSE project) for financial support.

References and notes

1. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1992**, *37*, 402.
2. Meier, H.; Lehmann, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 643.
3. Eckert, J.-F.; Nicoud, J.-F.; Nierengarten, J.-F. *J. Am. Chem. Soc.* **2000**, *122*, 7467.
4. El-ghayoury, A. P.; Schenning, H. J.; Van Hal, P. A.; Van Duren, J. K. J.; Janssen, R. A. J.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 3660.
5. Pron, A.; Rannou, P. *Prog. Polym. Sci.* **2002**, *27*, 135.
6. Zheng, M.; Sarker, A. M.; Gürel, E. E.; Lahti, P. M.; Karasz, F. E. *Macromolecules* **2000**, *33*, 7426.
7. Zyung, T.; Hwang, D.; Kang, I.; Shim, H.; Hwang, W.; Kim, J. *Chem. Mater.* **1995**, *7*, 1499.
8. Aguiar, M.; Karasz, F. E.; Akcelrud, L. *Macromolecules* **1995**, *28*, 4598.
9. Hay, M.; Klavetter, F. L. *J. Am. Chem. Soc.* **1995**, *117*, 7112.
10. Akcelrud, L. *Prog. Polym. Sci.* **2003**, *28*, 875.
11. Hochfilzer, C.; Rasch, S.; Winkler, B.; Huslage, J.; Leising, G. *Synth. Met.* **1997**, *85*, 1271.
12. Park, E. S.; Kim, H. S.; Kim, M. N.; Yoon, J. S. *Eur. Polym. J.* **2004**, *40*, 2819.
13. Kauffman, J. M.; Moyna, G. *J. Org. Chem.* **2003**, *68*, 839.
14. Meier, H.; Gerold, J.; Kolshorn, H.; Baumann, W.; Bletz, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 292.
15. General synthetic procedures: All the reagents and chemicals used for the syntheses were purchased from Aldrich. Solvents were of analytical, HPLC and anhydrous grade. The monomers, 4-methylstyrene and 4-chloromethylstyrene were passed through neutral alumina columns (Aldrich) to remove the inhibitor before use.
Synthesis of poly(4-methylstyrene-co-4-chloromethylstyrene), **P$_1$**: Methylstyrene (11.82 g, 0.1 mol), 1.53 g (0.01 mol) of chloromethylstyrene and benzoyl peroxide (240 mg) were dissolved in 20 mL of toluene in a reaction flask and purged with pure N_2 gas for 20 min. The flask was then placed on a preheated hotplate at 80 °C with stirring. Then the temperature was slowly raised to 130 °C. The reaction was allowed to proceed for 6 h under an N_2 atmosphere. The copolymer was precipitated by pouring into excess methanol, then filtered, purified by repeated reprecipitation from a solution of the polymer in toluene using methanol and dried at room temperature for 24 h. Elemental analysis conformed that copolymer **P$_1$** contains 3–3.5% of chlorine (calculated ~2.66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.1–6.5 (aromatic region), 4.52 (CH_2–Cl), 2.2–2.3 (CH_3–Ar).
Conversion of chloromethyl groups to phosphonate groups (copolymer ***P$_2$***): In a round bottom flask, 6 g of **P$_1$** and 10 mL of triethylphosphite (excess, ~10 times) were added and refluxed for 24 h at 140 °C with stirring.[7] The phosphonate polymer **P$_2$** was precipitated using a large excess of methanol and then filtered. Further purification of the product was carried out by dissolving in THF and reprecipitating using methanol. The product was then filtered and dried to give a white amorphous powder (yield 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.1–6.5 (aromatic region), 3.8–4.1 (Ar–PO–O_2–C_2H_4–C_2H_6), 2.95–3.12 (Ar–CH_2–PO–), 1.08–1.15

(Ar–PO–$\mathrm{O_2}$–$\mathrm{C_2H_4}$–C_2H_6), 2.2–2.3 (CH_3–Ar). Synthesis of hybrid polymer **10PMS-OPVC$_2$**: In a round bottom flask, 2 g of **P$_2$**, and 2 g of 4-(diethoxymethyl)benzaldehyde (~6 equiv) were dissolved in 50 mL of anhydrous THF. Potassium-*tert*-butoxide (1.5 g) was added and the flask was closed tightly and the reaction stirred at room temperature for 24 h under a nitrogen atmosphere.[8] The reaction mixture was precipitated using methanol and filtered. The product was dissolved in THF and reprecipitated using methanol to ensure complete removal of reagents. The product was then dissolved in 100 mL of THF containing 5 mL of 1 M HCl and stirred for 2–3 min to remove the aldehyde protection, precipitated using methanol, filtered and dried to give a pale yellow semi-crystalline powder (yield 95%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 9.7–9.94 (OHC–Ar), 6.2–7.3, 7.6–7.9, (aromatic region), 2.2–2.3 (CH_3–Ar).

Synthesis of 4-(diethoxyphosphorylmethyl)benzylchloride (**1**): α,α′-Dichloro-*p*-xylene (52.53 g, 0.3 mol) was taken in a round bottom flask containing a magnetic stirring bar. The flask was sealed using a rubber septum and immersed in an oil bath and the temperature was gradually raised to 120 °C to melt the compound. To the melt, 25 g (0.15 mol) of triethylphosphite was added slowly using a syringe over a period of 1 h with stirring. Needles were attached to the rubber septum before starting the addition of triethylphosphite, to avoid pressure building inside the flask. After the addition, the reaction was continued for 30 min. The progress of the reaction was monitored using thin layer chromatography in ethyl acetate. The reaction mixture was then cooled to room temperature to give a solid product. Purification was conducted by column chromatography using hexane–ethyl acetate (20 mL:80 mL) mixture to afford a viscous colourless liquid[9] (50% yield). Elemental analysis: C = 51.9%, H = 6.4%, Cl = 12.9% (calcd—C = 52.09%, H = 6.56%, Cl = 12.81%); Mass found—257 (M+H$^+$) (calcd—256.09); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 7.27–7.33 (m, 4H, Ar), 4.56 (s, 2H, Ar. CH_2–Cl), 3.99–4.03 (m, 4H, PO–$\mathrm{O_2}C_2H_4$–), 3.14 (d, 2H, $J = 21.9$ Hz, Ar–CH_2–PO), 1.24 (t, 6H, $J = 7.2$ Hz, PO–$\mathrm{O_2C_2H_4}$–C_2H_6).

Synthesis of (4-formyl-benzyl)-phosphonic acid diethyl ester (**2**): In a round bottom flask, 25 g (0.09 mol) of **1**, 25.33 g (0.181 mol) of hexamethylene tetraamine and 50 mL of 50% acetic acid were taken and the flask fitted with a reflux condenser. The mixture was refluxed under stirring for 3 h at 100 °C and then 15 mL of HCl was added and reflux continued for 15 min.[10] The mixture was then cooled to room temperature. The organic layer was extracted into DCM, dried using $\mathrm{MgSO_4}$ and evaporated to give a liquid. Purification was conducted by column chromatography using hexane–ethyl acetate (20 mL:80 mL). Compound **2** (21 g, yield 90%) was obtained as a viscous liquid. Elemental analysis: C = 55.5%, H = 6.6.l% (calcd—C = 56.25%, H = 6.69%); Mass found—277.14 (M+H$^+$) (calcd—276.07); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 9.97 (s, 1H, Ar–CHO), 7.79 (d, 2H, $J = 7.6$ Hz, Ar), 7.45–7.48 (m, 2H, Ar), 3.99–4.1 (m, 4H, PO–$\mathrm{O_2}C_2H_4$–), 3.14–3.22 (d, 2H, $J = 21.9$ Hz, Ar–CH_2–PO), 1.22–1.27 (t, 6H, $J = 7.2$ Hz, PO–$\mathrm{O_2C_2H_4}$–C_2H_6).

Synthesis of (4-diethoxymethyl-benzyl)-phosphonic acid diethyl ester (**m$_3$**): In a round bottom flask, 20 g of **2**, 23.1 g of triethyl orthoformate, 30–50 mL of ethanol and 400 mL of DCM were taken and stirred overnight at room temperature.[11] The reaction mixture was washed with cold 5% sodium hydroxide solution followed by water and the organic layer was extracted into DCM, dried using $\mathrm{MgSO_4}$ and evaporated. Purification was conducted by running column chromatography using hexane–ethyl acetate (20 mL:80 mL) to obtain **m$_3$** as a viscous colourless liquid (yield 95%). Elemental analysis: found—C = 57.89%, H = 8.37% (calcd—C = 58.1%, H = 8.24%); Mass found—331.1 (M+H$^+$) (calcd—330.16); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 7.42 (d, $J = 7.6$ Hz, 2H, Ar), 7.31 (d, $J = 7.6$ Hz, 2H, Ar), 5.51 (s, 2H, Ar–CH–O–), 4.00–4.11 (m, 4H, PO–$\mathrm{O_2}C_2H_4$–), 3.14 (d, 2H, $J = 21.9$ Hz, Ar–CH_2–PO), 1.22–1.26 (m, 12H, PO–$\mathrm{O_2C_2H_4}$–C_2H_6).

General synthetic procedure for **10PMS-OPVC$_n$** polymer hybrids: In a round bottom flask, 1.0 g of **10PMS-OPVC$_2$** and 2.0 g of **m$_3$** (~10 equiv) were dissolved in 50 mL of anhydrous THF. Potassium-*tert*-butoxide (1.25 g) was added and the reaction flask was closed tightly and reaction mixture stirred at room temperature for 24 h under a nitrogen atmosphere.[8] The product was precipitated using methanol and filtered. The product was dissolved in THF and reprecipitated using methanol to ensure complete removal of the reagents. The product was then dissolved in 100 mL of THF containing 5 mL of 0.1 M HCl and stirred for 2–3 min to remove the aldehyde protection, then precipitated using methanol, filtered and dried to obtain **10PMS-OPVC$_3$** as a yellow semi-crystalline product (yield 96%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 6.0–7.9 (aromatic region), 9.7–9.94 (OHC–Ar). The same experimental procedure was repeated step-wise to generate all the **10PMS-OPVC$_n$** ($n = 4$–9) polymer hybrids. The product obtained in one step was used as the starting material for the next step to obtain step by step OPV wiring.

Synthesis of **10PMS-OPV$_n$** polymer hybrids: In a general procedure, 50 mg of **10PMS-OPVC$_2$** and 200 mg of *diethyl-4-benzylphosphonate* (high excess) were dissolved in 10 mL of anhydrous THF. Potassium-*tert*-butoxide (100 mg) was added and the flask was closed tightly and the reaction stirred at room temperature for 24 h under an $\mathrm{N_2}$ atmosphere. The product was then precipitated using methanol and filtered.[8] The product was dissolved in THF and reprecipitated using methanol to ensure complete removal of the reagents. The product was precipitated using methanol, filtered and dried to give **10PMS-OPVC$_3$** as a yellow semi-crystalline product (yield 96%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ (ppm): 6.0–7.9 (aromatic region), 9.7–9.94 (OHC–Ar). A similar procedure was used for converting all **10PMS-OPVC$_n$** ($n = 4$–9) polymers to generate **10PMS-OPV$_n$** ($n = 4$–9) polymer hybrids.