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Investigation of different synthetic routes to and structure–property relationships of poly(*m*-phenylenevinylene-*co*-2,5-dioctyloxy-*p*-phenylenevinylene)†

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The synthesis of poly(*m*-phenylenevinylene-*co*-2,5-dioctyloxy-*p*-phenylenevinylene) by Horner–Emmons and Wittig condensation polymerisation in three different solvents is described. The chemical and optical properties of the derivatives thus formed are analysed, especially in relation to the differences in the *cis* : *trans* ratio of the vinylene bonds. Although they all have the same chemical composition, it is found that their chemical and optical properties vary. NMR studies show that the morphologies of the polymers are different, due to the differences in the *cis* : *trans* ratio of the vinylene bonds. It is found that the derivatives produced by Horner condensation contain a majority of *trans* bonds, and these derivatives show different spectral characteristics to the Wittig derivatives. The ability of the polymers to disperse carbon nanotubes is also studied. Here, not only is the synthetic route important, but the solvent used also plays a role. The derivatives that are produced by the Horner condensation route in DMF or chlorobenzene are found to have the best binding capabilities with carbon nanotubes.

Introduction

Poly(phenylenevinylene)s (PPVs) are widely used in the manufacture of optical and electrical devices because of their electroluminescent activity[1–3] and nonlinear optical responses.[4] By modifying the structure of PPV, various luminescent derivatives can be created that emit colours from the UV to the IR region. For example, introducing electron-donating groups onto the polymer unit leads to a red shift in the absorption maxima, while electron-withdrawing groups induce a blue shift.[5] These spectral shifts also modify the nonlinear optical response significantly.[4] Blue-shifted luminescence can also be achieved by reducing the effective conjugation of the main polymer chain. One way of doing this is by incorporating *meta*-linked phenyl rings within the backbone,[6] as in the case of the derivative poly(*m*-phenylenevinylene-*co*-2,5-dioctyloxy-*p*-phenylenevinylene). Solubility, and thus processability, is achieved by the introduction of the long alkoxy chains.[7]

A method to purify nanotubes has been developed in our group where pure nanotubes have been separated from unwanted impurities (such as soot and amorphous carbon produced in the Kraetchmer generator).[8,9] Composite films have also been made from polymer–nanotube solutions by traditional methods such as spin coating. These composites have been successively used as electron-transporting layers in optical light-emitting diodes.[10,11]

Various synthetic approaches to soluble dialkoxy PPVs have been reported in the literature, including the Gilch route,[12] the Wittig reaction,[13] aryl–ethylene coupling *via* Heck[4] or Suzuki reactions,[14] and the McMurray[15] and Wessling–Zimmermann route.[16] Polymers synthesised by these methods contain a number of structural defects as a result of incomplete elimination, cross-linking or other side reactions during polymerisation. Some of these reactions also have the disadvantage that alternating copolymers with different arylenevinylene units cannot be prepared. Both Wittig and Horner reactions involve heterocoupling processes and, therefore, these polycondensation routes are suitable for the synthesis of well-defined strictly alternating copolymers.

Previous studies on poly(arylenes) have suggested that there is a relationship between the optical properties and differences in the *cis* and *trans* isomers of the vinylene moiety.[17] Our studies show that the chemical and optical properties of poly(*m*-phenylenevinylene-*co*-2,5-dioctyloxy-*p*-phenylenevinylene) (P*m*PV) and its ability to disperse nanotubes vary with the *cis* : *trans* ratio and, thus, with the method used for its synthesis.[18] Atomistic computer simulation, combined with experimental observations, suggest that an all-*trans* configuration in the vinylene bonds facilitates dipolar binding between the polymer backbone and nanotubes.[19] Pfeiffer and Hörhold[20] have shown that those reactions using the Horner–Wadsworth–Emmons reaction yield primarily *trans* products. This has been confirmed by a study on the trimer 2,5-dioctyloxy-*p*-distyrylbenzene.[21] A systematic investigation of the synthesis has shown that not only the condensation method (Horner or Wittig), but also the reaction temperature and solvent employed affect the products.[22]

In this paper, the detailed synthesis of the polymer by Horner and Wittig condensation routes in three different solvents is described, and the chemical and optical properties of the polymers are compared.

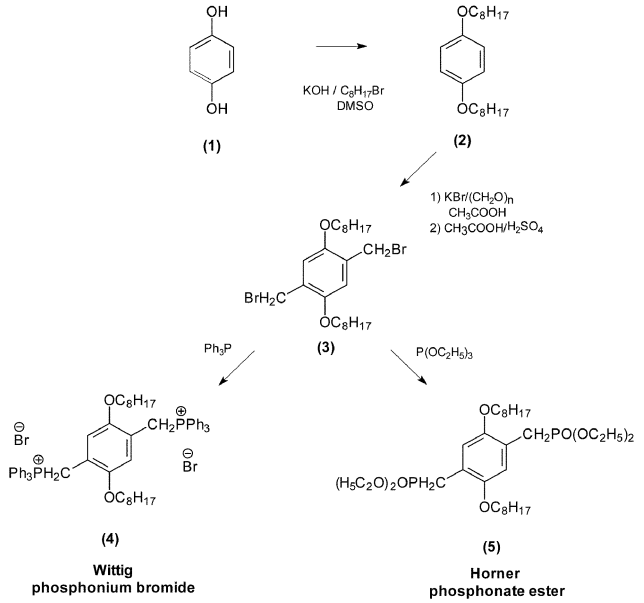
Results and discussion

Synthesis

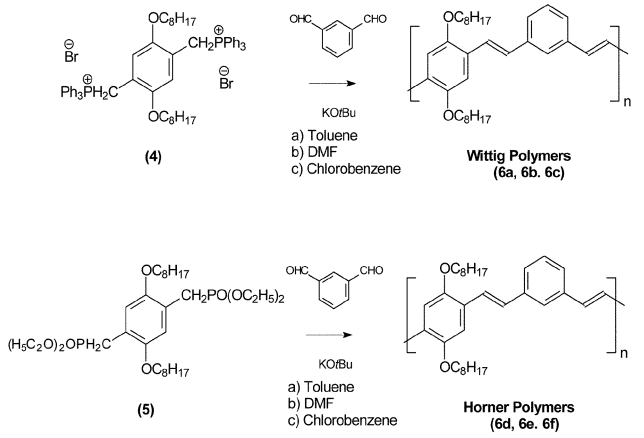
All polymers were produced by copolymerisation of isopthalaldehyde and either the Horner phosphonate ester or the Wittig phosphonium bromide. The synthetic routes employed are summarised in Schemes 1 and 2.

The starting materials were prepared in a three-step procedure (Scheme 1). The polymers were then made *via* Wittig- or Horner-type polycondensation (Scheme 2).

†Electronic supplementary information (ESI) available: synthesis and characterisation of starting materials **2**–**5**, and FTIR spectra of **6a**, **6c**, **6d**, and **6f**. See http://www.rsc.org/suppdata/jm/b2/b208439b/



Scheme 1 Synthesis of starting materials.



Scheme 2 Synthetic routes for synthesis of poly(*m*-phenylenevinylene-*co*-2,5-dioctyloxy-*p*-phenylenevinylene).

First, octyloxy side groups were introduced by a Williamson reaction of hydroquinone (**1**) with two equivalents of octylbromide.[23] The resulting 1,4-di-n-octyloxybenzene (**2**) was bromomethylated, using paraformaldehyde with potassium bromide in sulfuric and acetic acids, to give 2,5-di-n-octyloxy-1,4-bis(bromomethyl)benzene (**3**).[24,25] The Wittig salt was prepared by reacting **3** with two equivalents of triphenylphosphine in dry toluene to give 2,5-di-n-octyloxy-1,4-xylenebis(triphenylphosphonium bromide) (**4**),[26] whereas an Arbuzov reaction of **3** with triethyl phosphite yielded 2,5-di-n-octlyoxy-1,4-xylenebis(diethylphosphonate) (**5**).[27]

Three polymers were produced by Wittig olefination of **4** in dry toluene, dimethylformamide (DMF) and chlorobenzene.[13,27] They are designated as WTolP*m*PV (**6a**), WDMFP*m*PV (**6b**) and WCBP*m*PV (**6c**), repectively, where W stands for Wittig polycondensation and Tol, DMF and CB denote toluene, DMF and chlorobenzene, respectively. Similarly, three polymers were made by reacting phosphonate ester **5** in a Horner–Emmons polycondensation in dry toluene, DMF and chlorobenzene.[22,28] These are designated as HTolP*m*PV (**6d**), HDMFP*m*PV (**6e**) and HCBP*m*PV (**6f**), where H stands for Horner polycondensation and the solvents are indicated as before.

Table 1 Thermal properties of P*m*PVs

P*m*PV	T_g/°C	T_m[a] (side chain)/°C	T_m[a]/°C
WTol (**6a**)	50.5	70.2	92.6
WDMF (**6b**)	−0.76	63.4	88.8
WCB (**6c**)	12.5	Not detectable	Not detectable
HTol (**6d**)	9.5	46.7	85.8
HDMF (**6e**)	25.1	89.8	108.5
HCB (**6f**)	30.4	55.0	120.0

[a]T_m is measured from the peak maximum from the melting peak in the DSC thermogram.

Characterisation

The starting materials were characterised by NMR and FTIR spectroscopy, and elemental analysis. The polymers were characterised by NMR, FTIR, gel permeation chromotography (GPC), UV/Vis and photoluminescence (PL) spectroscopy, differential scanning calorimetry (DSC), and elemental analysis. The thermal properties of the polymers are summarised in Table 1.

All the polymers are polymorphic, as shown by the several endothermic transitions in their DSC thermograms. Transitions occurring at lower temperatures can be attributed to glass transitions and melting of the side chains, whereas at higher temperatures, melting of the polymer backbone occurs. These transitions are listed in Table 1 as T_g, T_m (side chain) and T_m, respectively. The temperature at which transitions occur depends on the properties of the molecule and, thus, on the method used to synthesise the polymer. The area under the melting peaks for HDMFP*m*PV and HCBP*m*PV are the largest amongst the series, which indicates that they have a greater percentage of crystallinity than the other polymers. The low T_g for WDMFP*m*PV can be attributed to trapped solvent (see Experimental). The molecular weight characteristics of the polymers are summarised Table 2.

The polymers showed large variations in molecular weight from M_w = 8600 to 46 000 and chain lengths, N_{av}, from 14 to 31 monomer units. WTolP*m*PV showed a variation in weight distribution. The mass profile consisted of a high molecular weight (M_w = 14 460) accompanied by two narrow bands of lower molecular weight, which are due to the presence of oligomers.

There was also some variation in polymer dispersity (from 1.3 to 3.5). As expected, the melting point range of the polymers showed an increase with higher molecular weight distribution and polydispersity. In each case, the polymers prepared by the Wittig route were of lower average molecular weight.

FTIR studies

FTIR spectroscopy was used to test the purity of the samples. All characteristic peaks for PPVs were present in the spectra of all six products and showed C–H and Ph–O–C stretching vibrations due to the alkoxy side chains attached to the phenyl ring. There was no evidence of the phosphonate ester starting

Table 2 Molecular weight characteristics of P*m*PVs

P*m*PV	M_w	M_n	M_w/M_n	N_{av}[a]
WTol (**6a**)	14 460	7890	1.8	17
WDMF (**6b**)	8650	6440	1.3	14
WCB (**6c**)	11 880	7710	1.5	17
HTol (**6d**)	38 640	14 460	2.7	31
HDMF (**6e**)	46 320	13 170	3.5	29
HCB (**6f**)	25 510	11 810	2.2	26

[a]N_{av} is the average chain length of the polymer and is obtained by dividing the number average molecular weight by the unit molecular weight.

material, characterised by the P=O stretch at 1280 cm^{-1}. The C–H out-of-plane vibration of the *meta*-phenylene ring occurs at 781 cm^{-1} and, in each case, there was a characteristic absorption between 961 and 964 cm^{-1} due to the *trans*-vinylene C–H out-of-plane vibration.

The assignment of the *cis*- and *trans*-vinylene modes is not agreed upon in the literature. Pang *et al.*[29] and Huang *et al.*[30] attribute the peak at 873 cm^{-1} to the *cis*-vinylene out-of-plane mode, while Dalton and co-workers[18] and Bradley[21] assign the peak occurring at 691 cm^{-1} to this vibration. However, the peak at 691 cm^{-1} could also be due to the deformation vibration of the *meta*-substituted phenyl ring.[31]

The present studies show that the intensities of the infrared absorptions of the peaks at 873 cm^{-1} and 691–694 cm^{-1} differ for the Horner and Wittig polymers. However it was not possible to make clear assignments and calculate *cis* : *trans* ratios from these peaks (see ESI† for spectra).

To investigate this further, one of the Wittig polymers (WTol) was converted to the pure *trans* isomer by refluxing in toluene in the presence of a catalytic amount of iodine. The elimination of the resonance signal at 3.5 ppm in the NMR spectrum indicated the conversion of *cis* bonds to *trans*; however, the peaks attributed to *cis* vibrations did not disappear in the IR spectrum, although the peak at 694 cm^{-1} was significantly reduced (see Fig. 1).

NMR studies

NMR was used to confirm the structure of the polymers. ^{13}C-NMR spectra indicate that the polymers prepared by each route are identical in chemical composition, but there are differences between the proton NMR spectra of the Horner and Wittig polymers. This is due to differences in the *cis* and *trans* orientation of the vinylene bonds of the polymers. The *trans*-vinylene protons occur as two doublets (with coupling constants of $J = 16$ Hz) between 7.10–7.20 and 7.48–7.55 ppm in all the polymers, whereas the *cis*-vinylene protons occur between 6.1–6.2 and 6.5–6.8 ppm in the Wittig polymers only. It was not possible to determine *cis*/*trans* ratios of these bonds due to broadening of NMR peaks; therefore, individual signals could not be integrated. However, the resonance at 4.1 ppm in the proton spectra, which is attributed to the OCH_2 groups of the alkoxy chains, is also affected by the *cis*/*trans* isomerism and results in a splitting of the signals into two signals at 3.5 and 4.1 ppm (due to *cis* and trans olefins, respectively). This is illustrated in Fig. 2 and 3, which show ^{1}H-NMR spectra of WCBPmPV (**6c**) before and after treatment with I_2, respectively.

The *cis*-CH=CH contents were estimated by integrating these signals in the spectra of the polymers and using the formula,

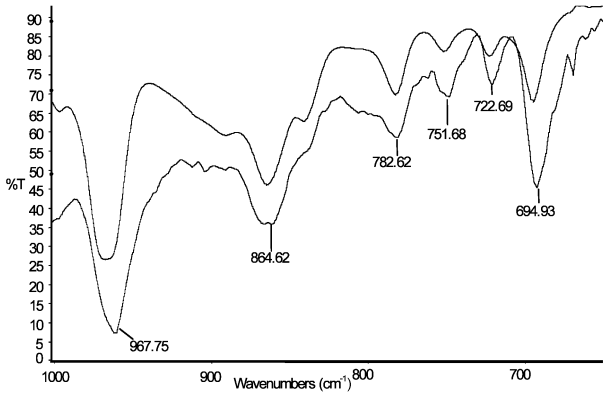


Fig. 1 Transmittance FTIR spectra for WTolP*m*PV (**6a**) before (lower trace) and after (upper trace) treatment with I_2.

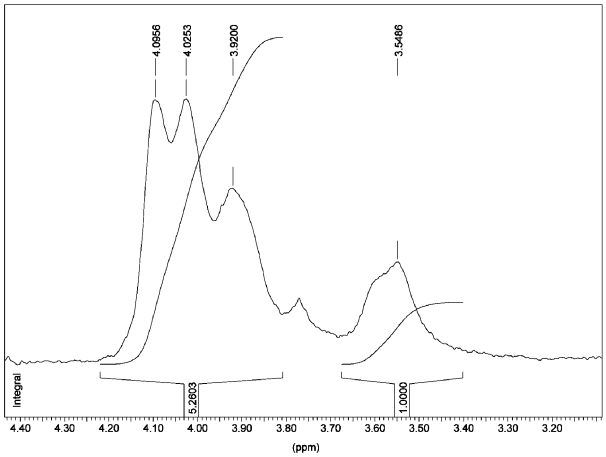


Fig. 2 ^{1}H-NMR resonances due to the OCH_2 groups of WCBP*m*PV (**6c**) before treatment with I_2.

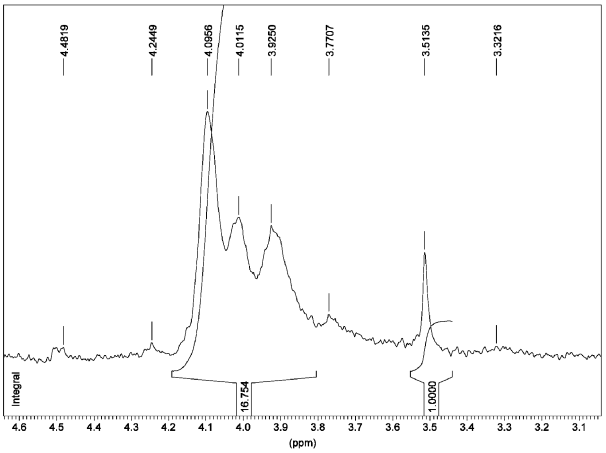


Fig. 3 ^{1}H-NMR resonances due to the OCH_2 groups of WCBP*m*PV (**6c**) after treatment with I_2.

$$\textit{cis}\ \text{Content}\ (\%) = 100[I_{cis}/(I_{cis} + I_{trans})]$$

where I is the sum of the integrations of the NMR signals. The percentage *cis* contents for each polymer are summarised in Table 3.

Generally, both routes produce derivatives containing a majority of thermodynamically more stable *trans* olefin bonds. While the Wittig method produces polymers with *cis* : *trans* ratios of around 1 : 4 to 1 : 6, the Horner route produces practically all *trans* bonds. These results agree with those obtained by Hörhold *et al.*[13,20]

Optical studies

Optical absorption and photoluminescent emission data for all the polymers are summarised in Table 4. Fig. 4 shows the UV/

Table 3 *cis* Contents of P*m*PVs from ^{1}H-NMR spectra

P*m*PV	OCH_2 (ppm)	I_{trans}	OCH_2 (ppm)	I_{cis}	*cis* Content (%)
WTol (**6a**)	4.15–3.91	3.86	3.51	1.0	20.6
WDMF (**6b**)	4.11–4.03	3.14	3.57	1.0	24.2
WCB (**6c**)	4.09–3.92	2.99	3.55	0.5	14.3
HTol (**6d**)	4.13–4.10	22.56	3.62	1.0	4.2
HDMF(**6e**)	4.11–4.10	92.24	3.61	1.0	1.1
HCB (**6f**)	4.12–4.10	41.54	3.60	1.0	2.4

Table 4 Optical properties of P*m*PVs

	λ/nm	
P*m*PV	UV/Vis absorption	PL emission
WTol (**6a**)	310, 385	449, 475, 520
WDMF (**6b**)	320, 391	448, 482, 520
WCB (**6c**)	342, 389	454, 482, 520
HTol (**6d**)	325, 405	453, 480, 520
HDMF (**6e**)	330, 405	454, 479, 520
HCB (**6f**)	330, 406	454, 482, 520

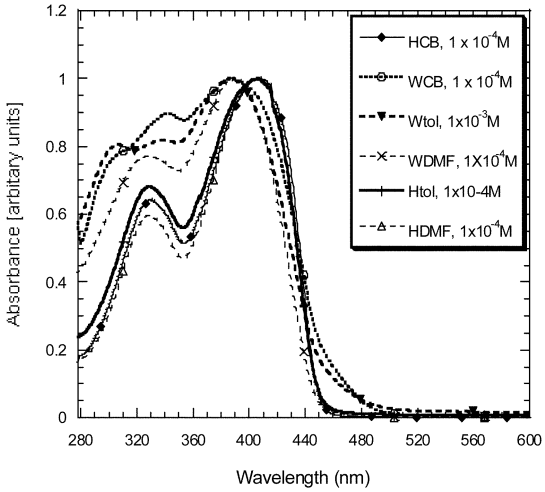


Fig. 4 UV/Vis absorption spectra of P*m*PV polymers (normalised to peak height) in toluene (1×10^{-4} M solutions).

Vis spectra (normalised to peak height) for 1×10^{-4} M toluene solutions of each type of polymer in 1 mm cuvettes. There are clear differences in spectral characteristics between the Wittig and Horner derivatives. Firstly, there is a blue shift in λ_{max} for the Wittig derivatives. As shown by the NMR studies reported here, the Wittig polymers have a higher ratio of *cis* linkages in the vinylene bond than the Horner polymers. It is plausible that this leads to disorder along the chain and consequent shortening of the conjugation length in the polymer backbone, thus giving rise to the blue shift observed. Secondly, the Wittig derivatives show the presence of a new feature just below 500 nm. Dalton and co-workers[18] have attributed this to the formation of an aggregate species, which may also be a consequence of the larger amount of *cis* bonds present in these derivatives, as the more random conformation caused by the increased amount of *cis* linkages leads to a greater amount of intra- and inter-chain interactions in the polymer strands. Further evidence for this comes from concentration-dependence studies carried out on HDMFP*m*PV and WTolP*m*PV.[22]

All the polymers show broadband photoluminescent emissions in the green–red region, with a peak at 450 nm and a second peak at 480 nm. (see Fig. 5). The second peak is more pronounced in WtolP*m*PV and is slightly red shifted. This behaviour is similar to that found in the concentration-dependence studies[18,22] mentioned above, which showed a red shift in the emission profile with increasing concentration. This is accounted for by re-absorption of the concentration-dependent absorption feature, causing an apparent red shift.

Conclusions

Poly(phenylenevinylene)s are important materials which are used in the manufacture of electronic, optical and electro-optical devices. Research in our group has focused on the purification of carbon nanotubes and on the fabrication of

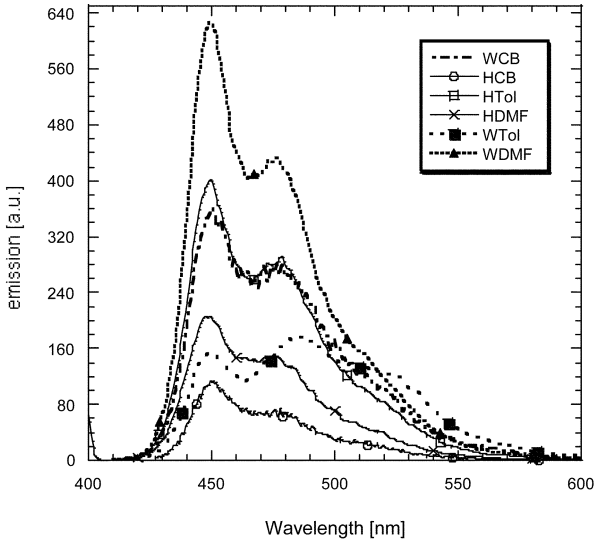


Fig. 5 PL emission spectra of P*m*PV polymers in toluene (1×10^{-5} M solutions).

carbon nanotube composites with conjugated polymers. Poly-(*m*-phenylenevinylene-*co*-2,5-dioctyloxy-*p*-phenylenevinylene) (P*m*PV) has been found to be one of the most useful materials for this purpose. All six polymers were tested for their ability to purify carbon nanotubes. It was found that HDMFP*m*PV and HCBP*m*PV showed the best purification properties and were the best candidates for fabrication of carbon nanotube composites.[32]

Modification of chemical structures to achieve the desired properties is well established. These studies show that the synthetic route employed for the preparation of P*m*PV can control the morphology of the polymer. This is particularly important for binding with carbon nanotubes, where an all-*trans* configuration of the vinylene bonds is important. We have also shown that nanotubes bind better to those polymers which have a higher degree of crystallinity (HDMFP*m*PV and HCBP*m*PV), which agrees well with other studies.[33,34]

Experimental

All experiments were carried out in oven-dried glassware. Commercially available chemicals were used without further purification. Anhydrous solvents were obtained from Sigma/Aldrich. The synthesis and characterisation of all the starting materials is described in the ESI†.

Measurements

Melting points were determined on a Griffin melting point apparatus (capillary method) and for the polymers by DSC using a Perkin-Elmer Pyris Diamond DSC at a heating rate of 20 K min^{-1} under an inert helium atmosphere. 5–10 mg of sample was measured in each case. Infrared spectra were measured on a Nicolet Continium FTIR-Microscope in reflectance mode; the sample was placed on an aluminium mirror. NMR spectra were recorded with a Bruker Advance DPX 400 MHz spectrometer as follows: ^{1}H-NMR at 400.1 MHz, internal standard TMS; ^{13}C-NMR at 100.6 MHz, internal standard deuterated solvent ($CDCl_3$); ^{31}P-NMR at 121.4 MHz. Molecular weights were determined by GPC using a Waters 600E pump with a Waters 486 tunable absorbance detector at 260 nm and employing the following 3.8 × 30 mm stryagel columns: HT3 (500 to 30 000 Å), HT5 (50 000 to 4×10^{60} Å), HT6E (5000 to 1×10^{7} Å). The polymers were injected into a 30 °C solution of tetrahydrofuran (THF) at a flow rate of 1 mL min^{-1}, and measured against polystyrene standards.

Solutions were filtered through a Millipore membrane with a porosity of 0.45 μm just before injection. Elemental analysis was carried out in the Microanalytical Laboratory of University College Dublin using a C440 EXITOR analytical elemental analyser. Absorption spectroscopy was performed with a Shimadzu UV-2101PC absorption spectrophotometer. All samples were measured in 1 mm quartz cells. Photoluminescence spectra were collected using a Perkin Elmer LS50B luminescence spectrophotometer (samples in 10 mm quartz cells).

Synthesis of polymers

WtolP*m*PV (6a). 2,5-Di-n-octyloxy-1,4-xylenebis(triphenylphosphonium bromide) (9.41 g, 9 mmol) and isophthalaldehyde (1.21 g, 9 mmol) were dissolved in 50 mL dry toluene at 110 °C. Potassium *tert*-butoxide (3.46 g, 31 mmol) was added in one portion and the mixture heated for a further 3.5 h. The toluene was evaporated under reduced pressure and the residue then dissolved in chloroform and filtered through phase separation paper. The filtrate was reduced to approx. 10 mL and the polymer precipitated by adding propanol. It was then collected, Soxhlet extracted in methanol overnight and dried to yield a red powder (1.7 g, 42%). M.p. 104–112 (capillary), 92.6 °C (DSC). Anal. calc. for $(C_{32}H_{44}O_2)_n$ (460.7)$_n$: C 83.43, H 9.63; found C 80.65, H 9.62%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm: 0.89 (t, 6H), 1.31–2.86 (m, 24H), 3.58 (t, 0.4H), 3.93–4.09 (t, 3H), 6.69–7.67 (m, 7H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ/ppm: 13.7 (C1), 22.2 (C2), 25.9 (C6), 28.9–29.1 (C7, C4, C5), 31.4 (C3), 69.2 (C8), 110.4 (C11), 123.4 (C16), 125.0 (C12, C15), 126.6 (C10), 128.4 (C17), 137.9 (C14), 150.7 (C9). UV/Vis (1×10^{-4} mol L^{-1} toluene solution) λ/nm: 310, 385. PL emission (1×10^{-5} mol L^{-1} toluene solution, excitation at 400 nm) λ/nm: 449, 475, 520 (shoulder). IR (microscope set-up) ν/cm^{-1}: 3046 (w), 3013 (w), 2938 (s), 2859 (s), 1937 (w), 1864 (w), 1803 (w), 1767 (w), 1709 (m), 1681 (w), 1593 (m), 1557 (w), 1505 (s), 1468 (m), 1418 (m), 1387 (m), 1341 (m), 1216 (s), 1121 (w), 1069 (m), 1044 (m), 970 (m), 858 (m), 808 (m), 781 (m), 749 (w), 722 (w), 694 (m). GPC (THF, 30 °C): M_w = 14 460, M_n = 7890.

WDMFP*m*PV (6b). 2,5-Di-n-octyloxy-1,4-xylenebis(triphenylphosphonium bromide) (9.41 g, 9 mmol) and isophthalaldehyde (1.21 g, 9 mmol) were dissolved in 50 mL dry DMF and heated under argon to 80 °C. Potassium *tert*-butoxide (3.46 g, 31 mmol) was added in one portion and the mixture heated for a further 3.5 h. The solution was then poured into 100 mL water and extracted with dichloromethane (100 mL × 2). The organic layer was dried ($MgSO_4$), filtered and reduced to approx. 10 mL. The polymer was precipitated with methanol several times but was difficult to obtain in powder form. This is probably due to trapped solvent. Eventually, a sticky yellow material was obtained (0.4 g, 10%). M.p. 88.8 °C (DSC). Anal. calc. for $(C_{32}H_{44}O_2)_n$ (460.7)$_n$: C 83.43, H 9.63; found C 80.65, H 9.62%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm: 0.89 (t, 6H), 1.25–1.93 (m, 28H), 4.00–4.13 (t, 3H), 3.51–3.77 (t, 2H), 6.54–7.67 (m, 10H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ/ppm: 14.1 (C1), 22.6 (C2), 26.2–26.3 (C6), 29.3–29.7 (C7, C4, C5), 31.8 (C3), 69.6 (C8), 110.5 (C11), 123.9 (C16), 125.3–125.4 (C12, C15), 127.4 (C10), 128.8 (C17), 138.4 (C14), 151.2 (C9). UV/Vis (1×10^{-4} mol L^{-1} toluene solution) λ/nm: 320, 391. PL emission (1×10^{-5} mol L^{-1} toluene solution, excitation at 400 nm) λ/nm: 448, 482, 520 (shoulder). IR (microscope set-up) ν/cm^{-1}: 3048 (m), 3012 (w), 2930 (s), 2853 (s), 2018 (w), 1931 (w), 1859 (w), 1796 (m), 1696 (m), 1624 (w), 1588 (s), 1506 (s), 1465 (m), 1424 (m), 1388 (m), 1337 (m), 1260(w), 1204 (s), 1208 (s), 1122 (w), 1030 (s), 963 (m), 896 (w), 840 (w), 794 (m), 718 (w), 692 (m). GPC (THF, 30 °C): M_w = 8650, M_n = 6440.

WCBP*m*PV (6c). The synthesis was carried out as for WDMFP*m*PV, using 9 mmol of each monomer and 50 mL dry chlorobenzene at 130 °C. The solution was then poured into 200 mL water and extracted with dichloromethane. The organic layer was dried, filtered and reduced to approx. 10 mL. The resulting product was precipitated out from methanol with difficulty, as again some solvent appeared to be trapped, providing a sticky orange material (0.4 g, 10%). M.p. 95–105 °C (capillary). Anal. calc. for $(C_{32}H_{44}O_2)_n$ (460.7)$_n$: C 83.43, H 9.63; found C 79.68, H 9.75% (the low value for C is probably due to trapped solvent).^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm: 0.89 (t, 6H), 1.31–2.89 (m, 26H), 3.57–4.10 (m, 4H), 6.67–7.66 (m, 8H).^{13}C-NMR (100 MHz, $CDCl_3$) δ/ppm: 14.0 (C1), 22.4 (C2), 26.2 (C6), 28.7 (C7, C4, C5), 2.1 (C3), 69.3 (C8), 110.9 (C11), 123.8 (C16), 125.8 (C12, C15), 126.5 (C10), 128.8 (C17), 137.9 (C14), 150.7 (C9). UV/Vis (1×10^{-4} mol L^{-1} toluene solution) λ/nm: 342, 389. PL emission (1×10^{-5} mol L^{-1} toluene solution, excitation at 400 nm) λ/nm: 454, 483, 520 (shoulder). IR (microscope set-up) ν/cm^{-1}: 2952 (s), 2924 (s), 2854 (s), 1626 (w), 1593 (m), 1574 (w), 1555 (w), 1546 (w), 1535 (w), 1500 (s), 1468 (s), 1418 (s), 1389 (m), 1340 (w), 1239 (w), 1205 (s), 1124 (w), 1043 (m), 1001 (w), 970 (m), 963 (m), 865 (m), 838 (w), 802 (w), 766 (w), 722 (w), 694 (m). GPC (THF, 30 °C): M_w = 11 880, M_n = 7710.

HTolP*m*PV (6d). 2,5-Di-n-octlyoxy-1,4-xylenebis(diethylphosphonate) (**5**; 12.9 g, 0.019 mol) and isophthalaldehyde (2.57 g, 0.019 mol) were added under argon to 100 mL dry toluene and heated with stirring to 110 °C. Potassium *tert*-butoxide (6.04 g, 0.054 mol) was added and the solution refluxed for a further 3.5 h. The toluene was evaporated under reduced pressure and the residue then dissolved in chloroform and filtered through phase separation paper. This was reduced to approx. 10 mL and the polymer precipitated by adding propanol. It was then collected, Soxhlet extracted in methanol overnight and dried to yield a bright yellow powder (3.2 g, 36%). M.p. 115–130 (capillary), 85.8 °C (DSC). Anal. calc. for $(C_{32}H_{44}O_2)_n$ (460.7)$_n$: C 83.43, H 9.63; found C 81.32, H 9.44%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm: 0.89 (t, 6H), 1.31–1.92 (m, 27H), 4.10–4.11 (t, 4H), 7.19–7.60 (m, 10H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ/ppm: 13.6 (C1), 22.2 (C2), 25.9 (C6), 28.9-29.1 (C7, C4, C5), 31.4 (C3), 69.3 (C8), 110.6 (C11), 123.5 (C16), 125.0 (C15), 126.6 (C10), 128.5 (C17), 137.9 (C14), 150.8 (C9). UV/Vis (1×10^{-4} mol L^{-1} toluene solution) λ/nm: 325, 405. PL emission (1×10^{-5} mol L^{-1} toluene solution, excitation at 437 nm) λ/nm: 453, 480, 520 (shoulder). IR (microscope set-up) ν/cm^{-1}: 3042 (m), 3012 (w), 2955 (s), 2858 (s), 1931 (w), 1854 (w), 1793 (m), 1721 (w), 1680 (m), 1629 (w), 1598 (s), 1506 (s), 1470 (m), 1429 (m), 1393 (m), 1337 (m), 1255 (s), 1214 (s), 1122 (w), 1046 (s), 968 (s), 897 (w), 871 (w), 810 (w), 784 (m), 723 (m), 692 (m). GPC (THF, 30 °C): M_w = 38 640, M_n = 14 460.

HDMFP*m*PV (6e). 2,5-Di-n-octlyoxy-1,4-xylenebis(diethylphosphonate) (**5**; 5.08 g, 8 mmol) and isophthalaldehyde (1.07 g, 8 mmol) were placed in a two-necked round-bottomed flask under argon and 100 mL dry DMF added. The solution was heated to 80 °C and potassium *tert*-butoxide (2.69 g, 24 mmol) was added in several portions (powder addition funnel). Heating at 80 °C under argon was continued for 3.5 h. The solution was then poured into 100 mL water and the aqueous solution extracted with toluene (100 mL × 2). The organic layer was then dried ($MgSO_4$) and concentrated to approx. 10 mL. Methanol was added to this to precipitate out the yellow product. This was then Soxhlet extracted with methanol overnight and dried under high vacuum to yield a yellow polymer (1.5 g, 42%). M.p. 125–140 (capillary), 108.5 °C (DSC). ^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm: 0.89 (t, 6H), 1.31–1.93 (m, 24H), 4.10–4.11 (t, 4H), 7.19–7.53 (m, 10H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ/ppm: 13.7 (C1), 22.2 (C2), 25.9

(C6), 28.9–29.1 (C7, C4, C5), 31.4 (C3), 69.2 (C8), 110.4 (C11), 123.4 (C16), 124.8 (C12), 126.5 (C10), 128.4 (C17), 137.9 (C14), 150.7 (C9). UV/Vis (1×10^{-4} mol L^{-1} toluene solution) λ/nm: 330, 405. PL emission (1×10^{-5} mol L^{-1} toluene solution, excitation at 434 nm) λ/nm: 454, 479, 520 (shoulder). IR (microscope set-up) ν/cm^{-1}: 3048 (m), 3017 (w), 2925 (s), 2853 (s), 1931 (w), 1854 (w), 1793 (m), 1696 (m), 1685 (m), 1588 (s), 1506 (s), 1465 (m), 1419 (m), 1393 (m), 1342 (m), 1193 (s), 1045 (s), 953 (s), 892 (w), 866 (w), 835 (w), 773 (m), 723 (w), 692 (m). GPC (THF, 30 °C): M_w = 46 320, M_n = 13 170.

HCBP*m*PV (6f). 2,5-Di-n-octlyoxy-1,4-xylenebis(diethylphosphonate) (**5**; 6.35 g, 10 mmol) and isopthalaldehyde (1.34 g, 10 mmol) and were heated to 130 °C in 70 mL dry chlorobenzene under nitrogen. Potassium *tert*-butoxide (3.18 g, 28 mmol) was added in one portion and the mixture heated for a further 3.5 h. The solution was then poured into 200 mL water and extracted with dichloromethane. The organic layer was dried, filtered and reduced to approx. 10 mL. The resulting product was precipitated out from methanol and dried to yield a yellow polymer (2.8 g, 62%). M.p. 128–145 (capillary), 120 °C (DSC). Anal. calc. for $(C_{32}H_{44}O_2)_n$ $(460.7)_n$: C 83.43, H 9.63; found C 80.64, H 9.64%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm: 0.89 (t, 6H), 1.31–1.93 (m, 27H), 4.10–4.11 (t, 4H), 7.19–7.67 (m, 10H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ/ppm: 13.6 (C1), 22.2 (C2), 25.8 (C6), 28.8–29.1 (C7, C4, C5), 31.4 (C3), 69.3 (C8), 110.5 (C11), 123.4 (C16), 124.8 (C12, C15), 126.6 (C10), 128.4 (C17), 137.9 (C14), 150.8 (C9). UV/Vis (1×10^{-4} mol L^{-1} toluene solution) λ/nm: 330, 406. PL emission (1×10^{-5} mol L^{-1} toluene solution, excitation at 434 nm) λ/nm: 454, 482, 520 (shoulder). IR (microscope set-up) ν/cm^{-1}: 3054 (m), 3010 (w), 2933 (s), 2856 (s), 2018 (w), 1930 (w), 1857 (w), 1797 (m), 1679 (m), 1593 (s), 1576 (w), 1499 (m), 1469 (m), 1422 (m), 1390 (m), 1340 (m), 1281 (w), 1244 (m), 1208 (s), 1124 (w), 1046 (s), 970 (s), 961 (s), 893 (w), 863 (w), 837 (w), 781 (m), 732 (w), 694 (m). GPC (THF, 30 °C): M_w = 25 510, M_n = 11 810.

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