ELECTRONIC SUPPLEMENTARY INFORMATION

Synthesis and photo-induced charge separation of confined conjugation length phenylene vinylene-based polymers

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Polymer Synthesis

Four confined chromophore polymers (PT3-6) were synthesised via a two-fold Horner Emmons reaction as depicted in Figure 1. The alkyl ether chain length was varied to systematically spatially separate the triphenylene chromophores. 1,4-bischloromethyl-2-methoxy-5-(2'-ethyl-hexyloxy) benzene **1** was synthesised according to literature procedure.[13] The pale yellow liquid was then heated to reflux in triethyl phosphite for 12 h and distilled under reduced pressure to give the bisphosphonate **2** as a clear viscous liquid. The linked dialdehydes **3-6** were synthesised by reacting 2 equivalents of *p*-hydroxybenzaldehyde with the respective dibromo alkane, under basic conditions. The fully conjugated polymer was synthesised via the same method but using terephthaldehyde and designated Alt-Co-MEH-PPV (an alternating copolymer of poly[*p*-(phenylene vinylene)-(2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-(phenylene vinylene)].

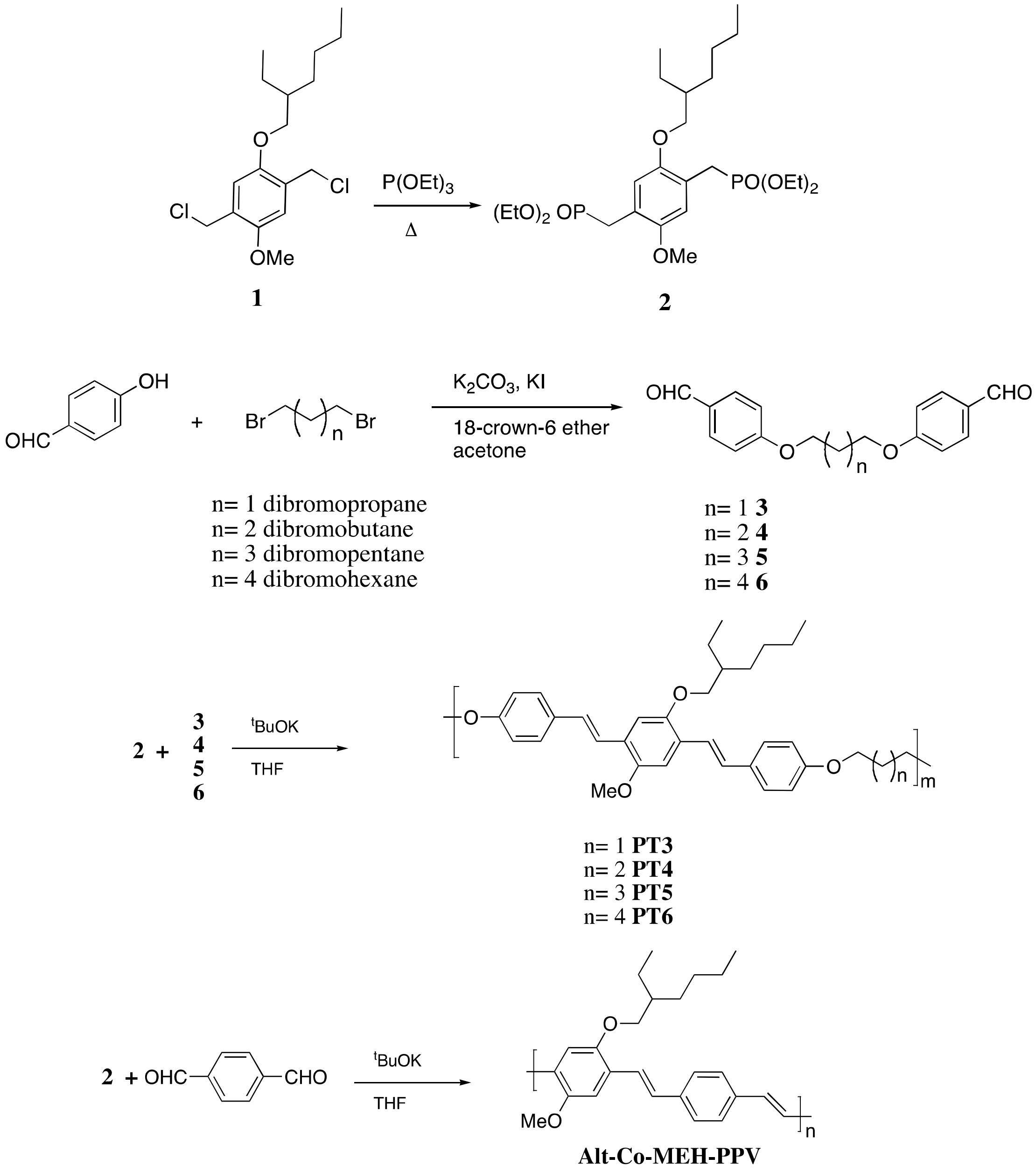

Figure 1: Synthesis of PT3-6 and Alt-Co-MEH-PPV

All reagents and solvents were of analytical grade and used as received from commercial suppliers. Anhydrous solvents were dried accordingly; methanol was refluxed over calcium hydride for 12 h, distilled under pressure and stored over 4 Å sieves under N_2 atmosphere. *N,N*-Dimethyl-formamide (DMF) was dried over calcium hydride and stored over 4 Å sieves under N_2 atmosphere. *Flash column chromatography* was performed on Merck Kieselgel 60 (230-400 mesh) silica. Analytical thin layer chromatography (TLC) was carried out on pre-coated 0.25 mm thick Merck 5715 Kieselgel 60 F_{254} silica gel plates and visualised under 254 nm or 366 nm ultraviolet light.

Nuclear Magnetic Resonance spectra. Proton nuclear magnetic resonance spectra (^{1}H NMR, 400 MHz and 500 MHz) and proton decoupled nuclear magnetic resonance spectra (^{13}C NMR, 100 MHz and 125 MHz) were recorded using residual dimethyl-d_6-sulphoxide (DMSO), d_4-methanol, d-chloroform and D_2O as internal standards on either a Varian Unity 400 or a Varian Unity 500. Chemical shift (δ) are reported in parts per million (ppm) and are followed by multiplicity, coupling constants (J) given in Hertz (Hz), integration and assignments. The following abbreviations have been used: s, singlet; d, doublet; dd, doublet of doublets; m, multiplets; br, broad.

Mass spectrometry. Electrospray ionisation (ESI) mass spectra (positive ion) were acquired on a Quattro II triple quadrupole instrument (Micromass, Manchester, UK) with an ion source operating at 80^0C and a cone voltage of 30 V. Samples were introduced to the source in a 1:1 mixture of filtered MilliQ water and acetonitrile solvents at 20 μl/min using a HP1100 LC system equipped with solvent degasser, binary pumps and autosampler (Hewlett Packard, Palo Alto, USA). Accurate ion mass spectrometry (High-resolution MS) were performed by ionising the sample via ESI, into a commercially available Finnigan LTQ FT hybrid mass spectrometer (Bremen Germany), using a linear ion trap and Fourier Transform Ion Cyclotron Resonance (FT-ICR).

Gel permeation chromatography (GPC) was carried out by Dr. Ming Chen, CSIRO Australia, using a Waters HPLC system calibrated with polystyrene standards, and HPLC grade THF as the eluent.

Infrared (IR) absorption spectra were recorded using a Perkin Elmer Spectrum One FT-IR spectrometer in neat solid or liquid state.

2-methoxy-5-(2-ethylhexyoxy)-1,4-xylylenebis(diethylphosphonate) (2)[40]

Bischloromethyl MEH **1** (3 g, 9 mmol) was refluxed neat in triethylphosphite for 12 h, after which excess triethylphosphite was removed via distillation (water pressure)

and then Kugelrohr distillation under reduced pressure was carried out to remove by-products to give the bisphosphonate as a viscous, pale yellow liquid (17.8 g, 60%)
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (s, 1H, *Ar-H*), 6.89 (s, 1H, *Ar-H*), 4.1-4.0 (m, 8H, OCH_2CH_3), 3.82-3.78 (m, 5H, O*Me*, OCH_2), 3.2-3.1 (2s, 4H, CH_2P) 1.58-0.9 (m, 27H, *MEH-H* and OCH_2CH_3).
^{13}C NMR (100 MHz, $CDCl_3$): 150.9, 119.6, 115.1, 114.2, 62.1, 56.9, 56.4, 42.0, 39.9, 30.8, 29.4, 27.3, 26.2, 25.8, 24.1, 23.2, 16.5, 14.3, 11.4.

General method for the preparation of dialdehydes (3-6)

4-hydroxybenzaldehyde (5 g, 40.9 mmol), 2.5 equivalents of dibromoalkane, 4 equivalents of K_2CO_3, trace amounts of KI and catalytic amounts of 18-crown-6 ether in acetone (150 ml) were refluxed under N_2 for 6 h. The solid was then filtered through celite and solvent concentrated *in vacuo*. The resultant mixture was then redissolved in DCM (60 ml) and washed with 15% KOH (3 x 60 ml) and then with water (3 x 50ml). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. Recrystallisation in EtOH gave the final bisaldehyde.

4,4’-propane-1,3-diylbis(oxy))dibenzaldehyde (3)

as white solid (8.6 g, 68%) **MP=** 120-121^{o}C
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.8 (s, 2H, *CHO*), 7.84-7.83 ((d, *J*= 18 Hz, 4H, *Ar-H*), 7.3-7.01 (d, *J*= 18 Hz, 4H, *Ar-H*), 4.25 (m, 4H, OCH_2), 2.35 (m, 2H, OCH_2CH_2)
^{13}C NMR (125 MHz, $CDCl_3$): 190.7, 163.7, 132.0, 130.0 114.7, 64.5, 29.0
High res. ESI-MS $[M+Na]^+$: 307.09415 Calculated = 307.09408

4,4’-butane-1,4-diylbis(oxy))dibenzaldehyde (4)

as white solid (10.5 g, 79%) **MP=** 102-104^{o}C
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 2H, *CHO*), 7.86-7.84 (d, *J*= 18 Hz, 4H, *Ar-H*), 7.23-7.09 (d, *J*= 18 Hz, 4H, *Ar-H*), 4.15 (m, 4H, OCH_2), 2.05 (m, 4H, OCH_2CH_2)
^{13}C NMR (125 MHz, $CDCl_3$): δ 190.7, 163.7, 144.7 132.0, 130.0, 67.7, 28.9
High res. ESI-MS $[M+Na]^+$: 321.10979 Calculated = 321.10973

4,4’-pentane-1,5-diylbis(oxy))dibenzaldehyde (5)

as white solid (9.6 g, 70%) **MP=** 110-112°C

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.88 (s, 2H, *CHO*), 7.84-7.82 (d, *J*= 18 Hz, 4H, *Ar-H*), 7.26 (d, *J*= 18 Hz, 4H, *Ar-H*), 4.15 (m, 4H, OCH_2), 1.93 (m, 4H, OCH_2CH_2), 1.69 (m, 2H, $OCH_2CH_2CH_2$)

^{13}C NMR (125 MHz, $CDCl_3$): δ 190.7, 164.1, 132.0, 129.9, 114.7, 68.1, 28.8, 22.7

High res. ESI-MS $[M+Na]^+$: 335.12549 Calculated = 335.12538

4,4’-hexane-1,6-diylbis(oxy))dibenzaldehyde (6)

as white solid (10.1 g, 70%) **MP=** 106-108°C

^{1}H NMR (500 MHz, $CDCl_3$): 9.88 (s, 2H, *CHO*), 7.83 (d, *J*= 18 Hz, 4H, *Ar-H*), 7.26 (d, *J*= 18 Hz, 4H, *Ar-H*), 4.06 (m, 4H, OCH_2), 1.93 (m, 4H, OCH_2CH_2), 1.69 (m, 4H, $OCH_2CH_2CH_2$)

^{13}C NMR (125 MHz, $CDCl_3$): δ 190.8, 164.1, 132.0, 129.9, 114.7, 68.2, 29.0, 25.7

High res. ESI-MS $[M+Na]^+$: 349.14109 Calculated= 349.14103

General Horner-Emmons polymerisation of confined length conjugation polymers (PT3-6)

Bisphosphonate **2** (1 g, 3.5 mmol) and one equivalent of dialdehyde, were dissolved in dry THF (40 ml) and purged with N_2 for 5 min and added to 10 equivalents of ^{t}BuOK suspended in pre-purged THF (20 ml). There was noticeable colour change to dark red as the ylide was formed and gradually became yellow. The reaction was allowed to stir for a further 18 h upon which the solvent was removed *in vacuo*. The solid was then dissolved into DCM and washed well with water. The organic layer was separated, dried over $MgSO_4$ and concentrated *in vacuo* to form a film in the round-bottom flask. MeOH was added to the flask and yellow solid precipitated. The solid was collected via centrifugation and redissolved in minimal DCM and reprecipitated with MeOH. The final product was collected via centrifugation to give the polymer as bright yellow solid.

Poly [1,3-propanedioxy-1,4- phenylene1,2-ethylene-((2-ethylhexyl)oxy, 5-methoxy-1,4- phenylene)-1,2-ethylene-1,4-phenylene] (PT3)

as bright yellow solid (0.23 g, 11%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.50–7.45 (m, *Ar-H*), 7.38-7.32 (m, *Ar-H),* 7.1 (m, ,*Ar-H*) 6.9 (br s, *olefinic-H*), 4.2 (br s, O*CH$_2$-aliphatic*), 3.94-3.91 (m, 5H, OCH$_2$ and OCH$_3$) 2.30 (m, 2H, OCH$_2$*CH$_2$-aliphatic*), 1.9-0.9 (m, *MEH-H*)

IR: cm^{-1} 2927, 2339, 1966, 1744, 1603, 1508, 1238, 1174, 1035, 965, 826

GPC: M$_w$= 9405, **PDI**= 1.73

UV-Vis λ$_{max}$: 393 nm

Emission λ$_{max}$: 448, 475 nm

Poly [1,4-butanedioxy-1,4- phenylene1,2-ethylene-((2-ethylhexyl)oxy, 5-methoxy-1,4- phenylene)-1,2-ethylene-1,4-phenylene] (PT4)

as bright yellow solid (0.21 g, 10%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.50–7.46 (m, *Ar-H*), 7.37-7.31 (m, *Ar-H),* 7.08 (m, *Ar-H*) 6.92 (br s, *olefinic-H*), 4.22 (br s, O*CH$_2$-aliphatic*), 3.95-3.93 (m, OCH$_2$ and OCH$_3$) 2.34 (m, OCH$_2$*CH$_2$-aliphatic*), 1.81-0.9 (m, *MEH-H*)

IR: cm^{-1} 2929, 2341, 1966, 1745, 1603, 1508, 1238, 1174, 1035, 965, 826

GPC: M$_w$= 12831, **PDI**= 1.99

UV-Vis λ$_{max}$: 393 nm

Emission λ$_{max}$: 448, 475 nm

Poly [1,5-pentanedioxy-1,4- phenylene1,2-ethylene-((2-ethylhexyl)oxy, 5-methoxy-1,4- phenylene)-1,2-ethylene-1,4-phenylene] (PT5)

as bright yellow solid (0.25 g, 12%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.49–7.42 (m, *Ar-H*), 7.34-7.31 (m, *Ar-H),* 7.10-7.03 (m, *Ar-H*) 6.89 (br s, *olefinic-H*), 4.55 (br s, O*CH$_2$-aliphatic*), 3.95-3.93 (m, OCH$_2$ and OCH$_3$) 1.88 (m, OCH$_2$*CH$_2$-aliphatic*), 1.79 (m, OCH$_2$CH$_2$*CH$_2$-aliphatic*), 1.67-0.92 (m, *MEH-H*)

IR: cm^{-1} 2930, 2349, 1967, 1744, 1601, 1508, 1238, 1171, 1038, 965, 826

GPC: M$_w$= 9362, **PDI**= 1.81

UV-Vis λ$_{max}$: 393 nm

Emission λ$_{max}$: 448, 475 nm

Poly [1,6-hexanedioxy-1,4- phenylene1,2-ethylene-((2-ethylhexyl)oxy, 5-methoxy-1,4- phenylene)-1,2-ethylene-1,4-phenylene] (PT4)

as bright yellow solid (0.23 g, 10%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.45–7.40 (m, *Ar-H*), 7.35-7.29 (m, *Ar-H)*, 7.11-7.07 (m, *Ar-H*) 6.91 (br s, *olefinic-H*), 4.20 (br s, O*CH$_2$-aliphatic*), 3.98-3.91 (m, OCH$_2$ and OCH$_3$) 1.89 (m, OCH$_2$*CH$_2$-aliphatic*), 1.73 (m, OCH$_2$CH$_2$*CH$_2$-aliphatic*), 1.70-0.91 (m, *MEH-H*)

IR: cm^{-1} 2927, 2339, 1973, 1749, 1601, 1508, 1238, 1174, 1033, 965, 826

GPC: M$_w$= 8915, **PDI**= 2.15

UV-Vis λ$_{max}$: 393 nm

Emission λ$_{max}$: 448, 475 nm

Poly- (2-methoxy 5-ethylhexyloxy-*p*-phenylene-vinylene)-*alt*-(*p*-phenylene vinylene) (Alt-Co-MEH-PPV)

Bisphosphonate **1** (1 g, 3.5 mmol) and one equivalent of terephthaldehyde, were dissolved in dry THF (40 ml) and purged with N$_2$ for 5 min and added to 10 equivalents of ^{t}BuOK suspended in pre-purged THF (20 ml). There was noticeable colour change to dark red as the ylide was formed and gradually became yellow. The reaction was allowed to stir for a further 18 h upon which the solvent was removed *in vacuo*. The solid was then dissolved in DCM (20 ml) and washed well with water (3 x 20 ml). The organic layer was separated, dried over MgSO$_4$ and concentrated *in vacuo* to form a film in the round-bottom flask. MeOH was added to the flask and yellow solid precipitated. The solid was collected via centrifugation and redissolved in minimal DCM and reprecipitated with MeOH. The final product was collected via centrifugation to give the polymer as bright orange solid (0.33 g, 14%)

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.55-7.32 (m, *Ar-H*), 7.14-7.04 (m, *Ar-H* and *olefinic-H*), 3.97-3.88 (m, *OCH$_3$* and *OCH$_2$*), 1.85-0.93 (br m, *MEH-H*)

IR cm^{-1} 2925, 1737, 1597, 1511, 1492, 1461, 1412, 1379, 1201, 1035, 958, 850, 708

GPC M$_w$: 12020, **PDI**= 1.67

UV-Vis λ$_{max}$: 403 nm

Emission λ$_{max}$: 446, 485, 524 nm