

All-*cis* Poly(phenylenevinylene)s from Titanium Mediated Reductions of Poly(phenyleneethynylene)s

Supporting Information

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TABLE OF CONTENTS

General Methods	S1–S2
General procedure for Sonogashiro reaction	S2–S3
General procedure for titanium mediated reduction	S3–S4
Substrate synthesis and characterization	S4–S13
Table of polymer properties	S11

General Methods

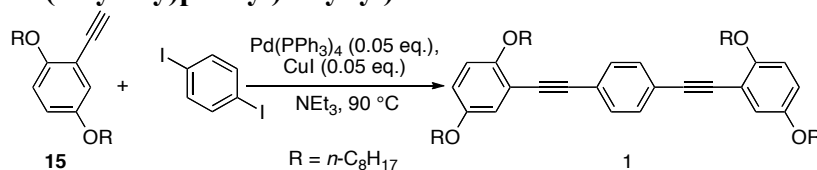
Unless otherwise noted, all reactions were performed under an oxygen-free atmosphere of argon using standard Schlenk-line techniques. Reaction solvents were dried using a Glasscontour dry solvent system, unless otherwise noted. Chemicals were used as received without further purification.

Fluorescence spectra were measured on a SPEX Fluorolog- τ 3 fluorimeter (model FL-321, 450 W Xenon lamp), the excitation wavelength used to obtain the fluorescence spectra corresponded to the absorption maxima in each case. Fluorescence quantum yields were determined by the optically dilute method¹ using perylene in ethanol and

¹ Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, 75, 991–1024.

were corrected for solvent refractive index and absorption differences at the excitation wavelength. Ultraviolet-visible absorption spectra were measured with an Agilent 8453 diode array spectrophotometer and corrected for background signal. Irradiation of polymers **16** and **17** was performed using a handheld Xe lamp (main wavelength: 365 nm) at a distance of *c.* 15 cm. ^1H and ^{13}C NMR were performed on a 500 MHz Varian instrument, in all cases the solvent used was deuteriochloroform (CDCl_3). Unless otherwise noted the reference peak was set to δ 7.27 and δ 77.23 ppm from tetramethylsilane for the ^1H and ^{13}C spectra respectively. Infrared (IR) spectra were recorded as a thin film on NaCl plates on a Perkin-Elmer Model 2000 FT-IR System transform spectrometer. High-resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APEXII 3 Tesla Fourier Transform Mass Spectrometer by the Massachusetts Institute of Technology Department of Chemistry Facility.

**General procedure for the Pd-catalyzed Sonogashiro Reaction:
1,4-Bis((2,5-bis(octyloxy)phenyl)ethynyl)benzene **1**:**

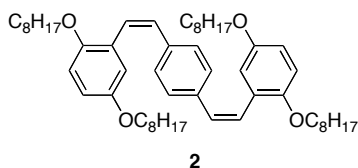


Alkyne **15** (300 mg, 0.84 mmole), 1,4-diiodobenzene (110 mg, 0.34 mmole), $\text{Pd(PPh}_3)_4$ (19 mg, 0.02 mmole) and copper (I) iodide (3.3 mg, 0.02 mmole) were combined with 5 mL triethylamine and then heated to reflux overnight. The reaction was cooled to room temperature, diluted with ethyl acetate, washed with saturated aqueous ammonium chloride (2x) and sodium chloride (brine, 1x), dried over magnesium sulfate, filtered and concentrated under reduced pressure on a rotary evaporator. The crude material was dissolved in DCM and dispersed on silica gel, the slurry was then concentrated under

reduced pressure and loaded onto a silica gel column. Chromatography (3:1 hexanes:DCM) provided an off white solid (140 mg, 53%). ^1H NMR (500 MHz, CDCl_3) δ 7.50 (s, 4H); 7.03 (d, J = 3.0 Hz, 2 H); 6.84 (m, 4 H); 4.02 (t, J = 6.5 Hz, 4H); 3.93 (t, J = 6.5 Hz, 4H); 1.84 (pent, J = 6.5 Hz, 4H); 1.77 (pent, J = 6.5 Hz, 4H); 1.54 (apparent pent, J = 7.6 Hz, 4H); 1.38 (m, 4H); 1.40–1.24 (bm, 32H); 0.89 (m, 12H); ^{13}C (125.8 MHz, CDCl_3) δ 154.3, 153.0, 131.6, 123.5, 118.5, 117.0, 114.2, 113.6, 93.2, 88.0, 70.0, 68.9, 32.0, 29.6, 29.6, 29.6, 29.5, 29.5, 26.3, 26.2, 22.9, 14.3; HRMS m/z (ESI, M^+) calcd 790.5895, found 790.5930.

General procedure for the Ti-mediated reduction of alkynes:

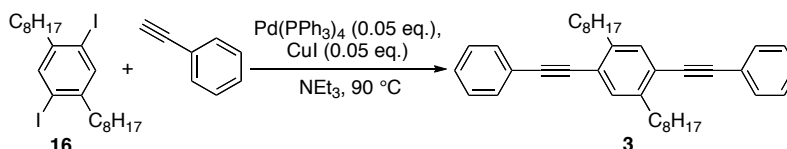
1,4-Bis(2,5-bis(octyloxy)styryl)benzene **2**:



Titanium isopropoxide (66 μL , 0.22 mmole) was added to a solution of **1** (25 mg, 0.03 mmole) in toluene (2.4 mL) and the reaction was cooled to $-78\text{ }^\circ\text{C}$. Isopropylmagnesium chloride (2 M in Et_2O , 200 μL , 0.40 mmole) was added in a single portion and the reaction was stirred for 30 minutes at $-78\text{ }^\circ\text{C}$ and then warmed to $-42\text{ }^\circ\text{C}$ for 3 hours. Water (200 μL) was added to the cooled solution, which was then warmed to room temperature and diluted with ethyl acetate (chloroform was used in the case of **13** and **16**). The organic layer was washed successively with 1M HCl and brine, dried over magnesium sulfate, filtered and concentrated. The crude solid was re-crystallized from diethyl ether and then filtered, rinsing with cold MeOH, to give 23 mg (23, 92%) of **2** as white crystals. Mp $77\text{--}79\text{ }^\circ\text{C}$; IR 2920 (s), 2851 (s), 1497 (m), 1471 (m), 1227 (s), 1046

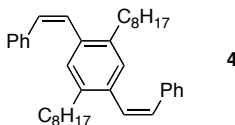
(m), 816 (m); ^1H NMR (500 MHz, CDCl_3) δ 7.13 (s, 4H); 6.79 (d, $J = 9.0$ Hz, 2H); 6.78 (d, $J = 3.0$ Hz, 2H); 6.72 (dd, $J = 9.0, 3.0$ Hz, 2H); 6.64 (d, $J = 12.3$ Hz, 2H); 6.52 (d, $J = 12.3$ Hz, 2H); 3.90 (t, $J = 6.6$ Hz, 4H); 3.66 (t, $J = 6.6$ Hz, 4H); 1.70 (pent, $J = 6.6$ Hz, 4H); 1.62 (pent, $J = 6.6$ Hz, 4H); 1.42 (m, 4H); 1.36–1.20 (bm, 36H); 0.89 (t, $J = 7.0$ Hz, 6H); 0.89 (t, $J = 7.0$ Hz, 6H); ^{13}C (125.8 MHz, CDCl_3) δ 152.7, 151.1, 136.2, 130.0, 128.8, 127.4, 125.8, 115.8, 115.3, 113.7, 69.4, 68.7, 32.0, 32.0, 29.6, 29.6, 29.6, 29.5, 29.5, 29.4, 26.3, 26.2, 22.9, 14.3; HRMS m/z (ESI, $\text{M}+\text{Na}^+$) calcd 817.6105, found 817.6100.

(2,5-Dioctyl-1,4-phenylene)bis(ethyne-2,1-diyl)dibenzene 3:



Following the same general procedure described for the synthesis of **1** provided **3** (466 mg, 74%) as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.55 (m, 4H); 7.38 (m, 8H); 6.84 (m, 4H); 2.83 (t, $J = 7.9$ Hz, 4H); 1.72 (pent, $J = 7.6$ Hz, 4H); 1.46–1.24 (bm, 20H); 0.89 (t, $J = 7.0$ Hz, 6H); ^{13}C (125.8 MHz, CDCl_3) δ 142.4, 132.5, 131.7, 128.6, 128.4, 123.7, 122.7, 94.1, 88.6, 34.4, 32.1, 30.9, 29.8, 29.7, 29.5, 22.9, 14.4; HRMS m/z (ESI, M^+) calcd 502.3594, found 502.3601.

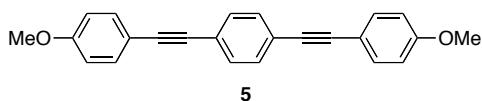
(1Z,1'Z)-2,2'-(2,5-Dioctyl-1,4-phenylene)bis(ethene-2,1-diyl)dibenzene 4:



According to the general procedure described for the synthesis of **2**, **4** (18 mg, 90%) was obtained after purification by silica-gel chromatography (hexanes). IR 2925 (s), 2854

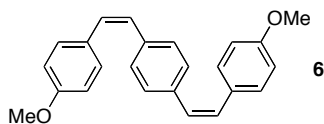
(m), 1447 (w), 919 (w), 775 (w), 694 (m); ^1H NMR (500 MHz, CDCl_3) δ 7.18 (m, 10H); 6.98 (s, 2H); 6.71 (d, $J = 12.0$ Hz, 2H); 6.60 (d, $J = 12.0$ Hz, 2H); 2.44 (t, $J = 7.9$ Hz, 4H), 1.38 (m, 4H); 1.30–1.16 (bm, 20 H); 0.87 (t, $J = 7.2$ Hz, 6H); ^{13}C (125.8 MHz, CDCl_3) δ 138.4, 137.3, 135.7, 130.5, 130.4, 129.8, 129.3, 128.2, 127.1, 33.2, 32.1, 30.8, 29.6, 29.6, 29.4, 22.9, 14.3; HRMS m/z (ESI, M^+) calcd 506.3907, found 506.3900.

1,4-Bis((4-methoxyphenyl)ethynyl)benzene **5**:



Diyne **5** was synthesized according to the procedure described by Weder and co-workers.² ^1H NMR (500 MHz, CDCl_3) δ 7.48 (s, 4H); 7.48 (d, $J = 9.0$ Hz, 4H); 6.89 (d, $J = 9.0$ Hz, 4H); 3.84 (s, 6H).

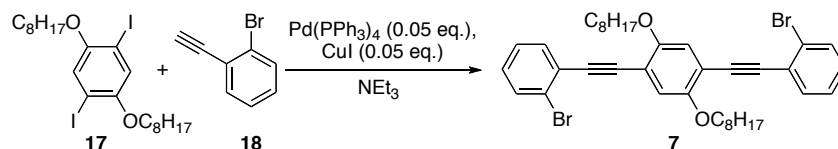
1,4-bis(4-methoxystyryl)benzene **6**:



According to the general procedure described for the synthesis of **2**, **6** (76 mg, 76%) was obtained as a colorless solid after re-crystallization from methanol. Mp 45–47 °C; IR 3005 (w), 2834 (w), 1606 (m), 1511 (s), 1462 (w), 1301 (w), 1252 (w), 1176 (m), 1033 (m), 833 (m); ^1H NMR (500 MHz, CDCl_3) δ 7.23 (d, $J = 8.7$ Hz, 4H); 6.78 (d, $J = 8.7$ Hz, 4H); 6.54 (d, $J = 12.2$ Hz, 2H); 6.48 (d, $J = 12.2$ Hz, 2H); 3.81 (s, 6H); ^{13}C (125.8 MHz, CDCl_3) δ 158.8, 136.4, 130.3, 129.9, 128.9, 128.7, 113.7, 100.0, 55.4; HRMS m/z (ESI, $\text{M}+\text{Na}^+$) calcd 365.1512, found 365.1501.

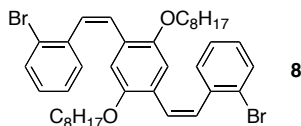
² Palmans, A. R. A.; Eglin, M.; Montali, A.; Weder, C.; Smith, P. *Chem. Mater.* **2000**, *12*, 472–480.

Dibromo-triaryl-diyne **7**:



The coupling of **17** and **18** was performed in a manner analogous to the procedure described in the synthesis of **1** (except the reaction was run at room temperature), to give **7** as an off white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.63 (d, $J = 8.0$ Hz, 2H); 7.58 (dd, $J = 8.0, 1.5$ Hz, 2 H); 7.30 (t, $J = 8.0$ Hz, 2H); 7.19 (dt, $J_t = 8.0$ Hz, $J_d = 1.5$ Hz, 2H); 7.06 (s, 2H); 4.05 (t, $J = 6.5$ Hz, 4H); 1.86 (pent, $J = 6.5$ Hz, 4H); 1.54 (pent, $J = 7.5$ Hz, 4H); 1.38–1.23 (bm, 16H); 0.88 (t, $J = 7.5$ Hz, 6H); ^{13}C (125.8 MHz, CDCl_3) δ 154.0, 133.6, 132.7, 129.6, 127.2, 125.8, 125.6, 117.2, 114.1, 95.6, 90.7, 69.9, 32.0, 29.7, 29.6, 29.5, 26.4, 22.9, 14.3.

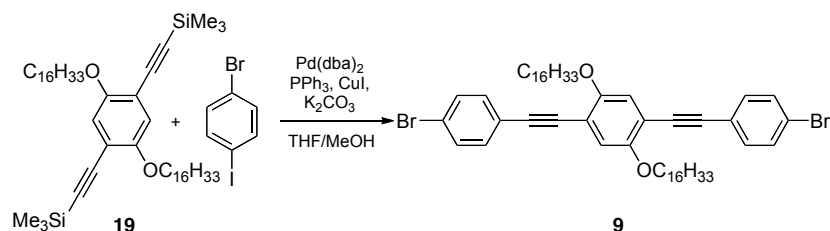
Dibromo-triaryl-diene **8**:



According to the general procedure described for the synthesis of **2**, diyne **7** (138 mg, 0.20 mmole) provided, after chromatography (50:1 hexanes:ethyl acetate) and re-crystallization (ethanol), **8** as pale yellow crystals (96 mg, 69%). IR 2925 (s), 2855 (m), 1463 (s), 1423 (s), 1206 (s), 1025 (s), 749 (s); ^1H NMR (500 MHz, CDCl_3) δ 7.59 (dd, $J = 7.9, 1.2$ Hz, 2 H); 7.22 (dd, $J = 7.7, 1.6$ Hz, 2 H); 6.81 (d, $J = 12.1$ Hz, 2H); 6.62 (d, $J = 12.1$ Hz, 2H); 6.46 (s, 2H); 3.40 (t, $J = 6.7$ Hz, 4H); 1.52 (m, 4H); 1.33–1.25 (bm, 20H); 0.91 (t, $J = 7.0$ Hz, 6H); ^{13}C (125.8 MHz, CDCl_3) δ 150.3, 138.7, 131.2, 129.3, 128.6,

127.2, 126.6, 125.5, 124.1, 114.1, 68.8, 32.1, 29.5, 29.5, 29.2, 26.1, 22.9, 14.4; HRMS m/z (ESI, $M+Na^+$) calcd 717.1913, found 717.1890.

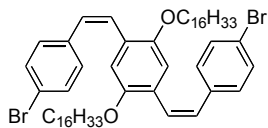
Dibromo-triaryl-diyne 9:



The synthesis of **9** was accomplished according to the procedure described by Tour and co-workers.³ To a flask containing silyl-terminated diyne **19** (842 mg, 1.12 mmole) 1-bromo-4-iodobenzene (760 mg, 2.69 mmole), bis(dibenzylideneacetone)palladium(0) (77 mg, 0.13 mmole), triphenylphosphine (70 mg, 0.27 mmole), and potassium carbonate (929 mg, 6.7 mmole) was added THF (16 mL) and methanol (4 mL). The flask was sealed with a rubber septum and stirred at room temperature overnight. The crude mixture was filtered through a plug of silica, eluting with dichloromethane, and then washed with 1 M HCl and brine. The organic layer was dried over magnesium sulfate, filtered, concentrated and subject to silica gel chromatography (50:1 hexanes:Et₂O) to give **9** as a yellow solid (871 mg, 84%). IR 2919 (s), 2848 (s), 2208 (w), 1504 (m), 1466 (m), 1219 (s), 1068 (m), 822 (s); ¹H NMR (500 MHz, CDCl₃) δ 7.48 (d, J = 8.6 Hz, 4H); 7.39 (d, J = 8.6 Hz, 4H); 7.00 (s, 2H); 4.02 (t, J = 6.4 Hz, 4H); 1.84 (p, J = 7.8 Hz, 4H); 1.53 (p, J = 7.7 Hz, 4H); 1.37 (m, 4H); 1.26 (bm, 44H); 0.88 (t, J = 7.5 Hz, 6H); ¹³C (125.8 MHz, CDCl₃) δ 153.8, 133.2, 131.8, 122.7, 122.6, 116.9, 114.0, 94.1, 87.3, 69.8, 32.2, 29.9, 29.9, 29.8, 29.6, 29.6, 29.5, 26.3, 22.9, 14.4.

³ Huang, S.; Tour, J. M. *Tetrahedron Lett.* **1999**, *40*, 3347-3350.

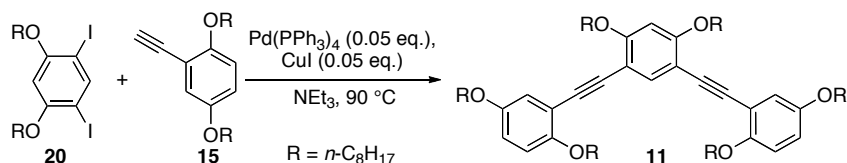
Dibromo-triaryl-diene **10**:



10

According to the general procedure described for the synthesis of **2**, diyne **9** (275 mg, 0.30 mmole) provided, after re-crystallization from hot ethanol/DCM, **10** as pale yellow crystals (229 mg, 82%). IR 2918 (s), 2850 (s), 1471 (s), 1422 (s), 1210 (s), 1023 (s), 1010 (s), 839 (s) 719 (m); ^1H NMR (500 MHz, CDCl_3) δ 7.36 (d, $J = 8.4$ Hz, 4H); 7.16 (d, $J = 8.4$ Hz, 4H); 6.78 (d, $J = 12.2$ Hz, 2H); 6.64 (s, 2H); 6.53 (d, $J = 12.2$ Hz, 2H); 3.54 (t, $J = 6.7$ Hz, 4H); 1.55 (p, $J = 7.2$ Hz, 4H); 1.32–1.24 (bm, 52H); 0.89 (t, $J = 7.0$ Hz, 6H); ^{13}C (125.8 MHz, CDCl_3) δ 150.3, 136.8, 131.8, 131.4, 130.8, 129.0, 126.5, 126.1, 121.0, 114.2, 69.1, 32.2, 29.9, 29.9, 29.9, 29.8, 29.6, 29.5, 29.3, 26.1, 22.9, 14.4. HRMS m/z (ESI, $\text{M}+\text{Na}^+$) calcd 943.4417, found 943.4427.

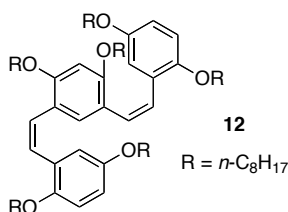
1,3-diyne **11**:



The coupling of **20** (260 mg, 0.44 mmole) and **15** (350 mg, 0.98 mmole) was performed in a manner analogous to the general procedure described in the synthesis of **1**, to give **11** as a yellow solid after purification by silica-gel chromatography. ^1H NMR (500 MHz, CDCl_3) δ 7.61 (s, 1H); 7.01 (t, $J = 1.5$ Hz, 2 H); 6.81 (d, $J = 8.0$ Hz, 2H); 6.80 (d, $J = 8.0$ Hz, 2H); 6.42 (s, 1H); 4.08 (t, $J = 6.7$ Hz, 4H); 4.02 (t, $J = 6.7$ Hz, 4H); 3.91 (t, $J = 6.6$ Hz, 4H); 1.88 (pent, $J = 7.2$ Hz, 4H); 1.83 (pent, $J = 7.9$ Hz, 4H); 1.76 (pent, $J = 7.9$ Hz,

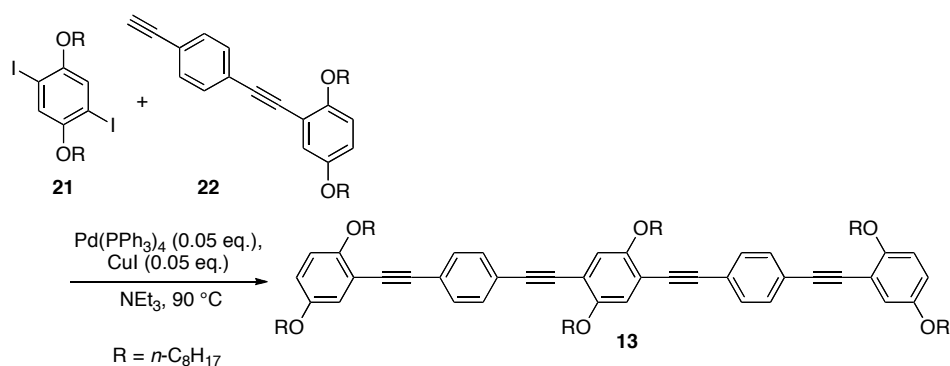
4H); 1.55–1.42 (m, 12H); 1.40–1.20 (bm, 48H); 0.90 (t, $J = 7.0$ Hz, 3H); 0.87 (t, $J = 7.0$ Hz, 3H); 0.84 (t, $J = 7.0$ Hz, 3H); ^{13}C (125.8 MHz, CDCl_3) δ 161.1, 154.0, 153.0, 137.8, 118.7, 116.1, 114.8, 114.7, 105.9, 97.8, 89.3, 89.0, 70.2, 69.3, 68.8, 32.0, 32.0, 29.6, 29.6, 29.6, 29.6, 29.5, 29.5, 29.5, 29.5, 29.4, 26.3, 26.2, 26.2, 22.9, 22.9, 14.3, 14.3; HRMS m/z (ESI, $\text{M}+\text{Na}^+$) calcd 1069.8195, found 1069.8151.

1,3-*Cis*-diene **12**;



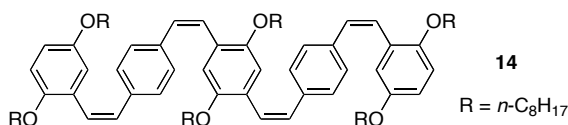
According to the general procedure described for the synthesis of **2**, diyne **11** (42 mg, 0.04 mmole) provided, after chromatography (30:1 hexanes:ethyl acetate), 42 mg (99%) of **12** as an amorphous solid. IR 2925 (s), 2855 (s), 1604 (m), 1492 (s), 1465 (s), 1391 (m), 1300 (s), 1223 (s), 1092 (m), 1048 (m), 876 (w), 778 (w); ^1H NMR (500 MHz, CDCl_3) δ 7.23 (s, 1H); 6.74 (d, $J = 2.9$ Hz, 2H); 6.68 (d, $J = 8.9$ Hz, 2H); 6.62 (dd, $J = 8.9, 3.0$ Hz, 2H); 6.57 (d, $J = 12.3$ Hz, 2H); 6.50 (d, $J = 12.3$ Hz, 2H); 6.36 (s, 1H); 3.87 (t, $J = 6.6$ Hz, 4H); 3.81 (t, $J = 6.6$ Hz, 4H); 3.59 (t, $J = 6.6$ Hz, 4H); 1.71 (m, 4H); 1.66 (m, 4H); 1.57 (m, 4H); 1.46–1.20 (bm, 60H); 0.90 (m, 18H); ^{13}C (125.8 MHz, CDCl_3) δ 157.0, 152.6, 151.0, 131.0, 127.9, 124.6, 123.9, 118.6, 115.3, 114.8, 113.8, 97.1, 69.7, 68.8, 68.7, 32.1, 32.1, 29.7, 29.7, 29.7, 29.6, 29.5, 29.5, 29.5, 29.4, 26.4, 26.3, 22.9, 22.9, 14.3; HRMS m/z (ESI, M^+) calcd 1050.8610, found 1050.8626.

Tetrayne **13**:



The coupling of **21** (185 mg, 0.32 mmole) and **22** (333 mg, 0.73 mmole) was performed in a manner analogous to the general procedure described for the synthesis of **1**, to give **13** as a bright yellow solid after chromatography (2:1 hexanes:DCM). ^1H NMR (500 MHz, CDCl_3) δ 7.51 (s, 8H); 7.03 (bs, 4H); 6.85 (m, 4H); 4.05 (t, $J = 7.2$ Hz, 4H); 4.02 (t, $J = 6.5$ Hz, 4H); 3.93 (t, $J = 6.5$ Hz, 4H); 1.86 (m, 8H); 1.77 (pent, $J = 7.9$ Hz, 4H); 1.55 (m, 8H); 1.45 (m, 4H); 1.42–1.24 (m, 48H); 0.88 (m, 18H); ^{13}C (125.8 MHz, CDCl_3) δ 154.4, 153.8, 153.0, 131.6, 131.6, 123.8, 123.2, 118.5, 117.0, 114.2, 114.1, 113.5, 100.0, 95.0, 93.2, 88.2, 88.0, 70.0, 69.8, 68.9, 32.0, 29.6, 29.6, 29.6, 29.6, 29.5, 29.5, 26.3, 26.3, 26.2, 22.9, 22.9, 14.3; HRMS m/z (ESI, M^+) calcd 1247.9001, found 1247.9042.

Tetra-*Z*-ene **14**:



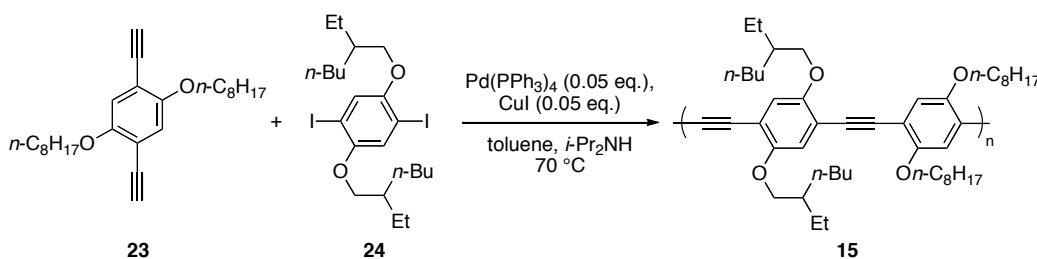
According to the general procedure described for the synthesis of **2**, tetrayne **13** (50 mg, 0.04 mmole) provided, after chromatography (3:1 hexanes:DCM), 33 mg (66%) of **14** as an bright yellow solid. IR 2918 (s), 1494 (m), 1469 (m), 1392 (m), 1224 (s), 1035 (m); ^1H NMR (500 MHz, CDCl_3) δ 7.16 (m, 8H); 6.77 (m, 8H); 6.65 (d, $J = 12.0$ Hz, 2H);

6.63 (d, $J = 12.0$ Hz, 2H); 6.52 (d, $J = 12.0$ Hz, 2H); 6.51 (d, $J = 12.0$ Hz, 2H); 3.90 (t, $J = 6.5$ Hz, 4H); 3.66 (t, $J = 6.5$ Hz, 4H); 3.54 (t, $J = 6.5$ Hz, 4H); 1.71 (m, 4H); 1.61 (m, 4H); 1.56 (m, 4H); 1.40–1.20 (m, 60 H); 0.88 (m, 18H); ^{13}C (125.8 MHz, CDCl_3) δ 152.7, 151.2, 150.3, 136.4, 129.9, 129.7, 128.9, 128.8, 127.4, 126.4, 125.5, 115.9, 115.2, 114.1, 113.7, 69.5, 69.0, 68.7, 32.0, 32.0, 29.9, 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, 26.3, 26.2, 22.9, 22.9, 14.4, 14.3; HRMS m/z (ESI, M^+) calcd 1254.9549, found 1254.9513.

Table S1: Polymer properties

Polymer	M_n (kDa)	PDI	λ_{max} (abs) (nm)		λ_{max} (em) (nm)		quantum yield (THF)
			THF	thin film	THF	thin film	
15	103	5.3	449	474	472	491	82%
16	61	4.0	419	411	533	542	29%
17	24	2.5	405	420	488	508	86%

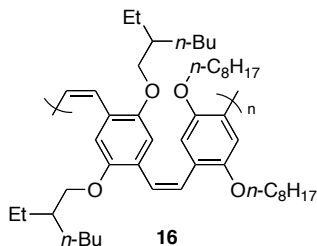
PPE 15:



Under inert atmosphere **23** (78 mg, 0.20 mmole) and **24** (117 mg, 0.20 mmole) were added to a sealed flask, followed by toluene (12 mL), $\text{Pd(PPh}_3)_4$ (5.4 mg, 0.010 mmole), CuI (2 mg, 0.010 mmole) and diisopropylamine (4 mL). The vessel was sealed and stirred at 70 °C within the glovebox for 72 hours. After removing the vessel from the glovebox and cooling to room temperature water was added to the reaction mixture. The product was extracted with chloroform (3x) and the combined organics were washed with

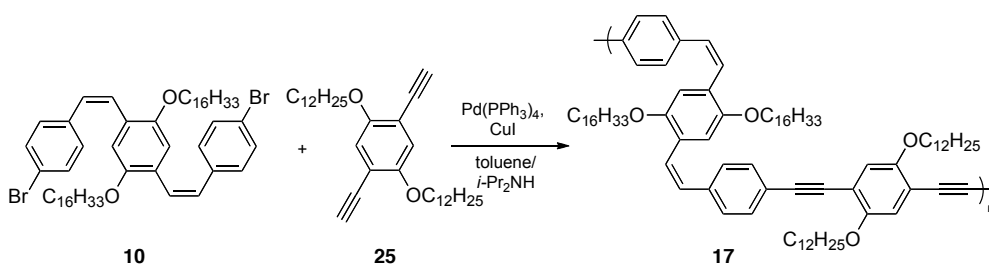
0.05 M HCl, dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was re-dissolved in chloroform and then precipitated out of solution *via* the addition of methanol. The precipitate was filtered off, air dried and then re-dissolved in chloroform and re-precipitated with methanol. The process was repeated a third time and the yellow solid was then rinsed with hot acetone, collected and dried *in vacuo*, giving 90 mg (63%) of a yellow polymer. IR 2925 (s), 2858 (s), 2364 (w), 1512 (m), 1466 (m), 1425 (m), 1381 (m), 1274 (m), 1466 (m), 1425 (m), 1381 (m), 1274 (m), 1213 (s), 1032 (m), 866 (w); ¹H NMR (500 MHz, CDCl₃) δ 7.02 (bs, 4H); 4.03 (m, 4H); 3.93 (m, 4H); 1.87 (m, 6H); 1.53 (bm, 8H); 1.40–1.20 (m, 20H); 0.97 (m, 6H); 0.88 (m, 12H).

All-*cis* PPV 16:



According to the general procedure described for the synthesis of **2**, with the notable exception that the reaction and purification were performed in the absence of light, polymer **15** (5 mg) was reduced to **16**, which was isolated by re-precipitation (3x) from toluene/methanol and was washed with hot acetone giving **16** as a red film (4.3 mg, 86%). IR 2924 (s), 2854 (s), 1741 (w), 1469 (m), 1417 (m), 1381 (m), 1265 (w), 1205 (m), 1051 (m), 870 (w), 804 (w); ¹H NMR (500 MHz, CDCl₃) δ 6.81 (m, 7H); 3.93 (m, 2H); 3.53 (m, 6H); 1.82–1.38 (bm, 42H); 0.87 (m, 18H); ¹³C (125.8 MHz, CDCl₃) δ 150.5, 150.3, 126.3, 126.2, 124.9, 114.0, 71.6, 69.1, 39.5, 32.1, 30.7, 29.9, 29.3, 29.0, 26.3, 24.1, 24.0, 23.4, 22.9, 14.4, 14.3, 11.3.

Cis-PPV/PPE 17:



Following the same polymerization procedure as described for **15** provided **17** (39 mg, 62%) from **10** (46 mg, 0.05 mmole) and **25** (25 mg, 0.05 mmole). IR 2924 (s), 2853 (s), 2207 (w), 1515 (m), 1495 (m), 1468 (m), 1209 (s), 1030 (m), 846 (m), 721 (w); ^1H NMR (500 MHz, CDCl_3) δ 7.58–7.15 (m, 9H); 7.01 (m, 2H); 6.80–6.50 (m, 5H); 4.03 (bs, 5H); 3.57 (bs, 3H); 1.85 (bm, 5H); 1.57 (bm, 7H); 1.40–1.16 (bm, 84H); 0.88 (bs, 12H); ^{13}C (125.8 MHz, CDCl_3) δ 153.8, 150.4, 137.9, 136.8, 131.7, 131.5, 131.4, 130.8, 129.1, 126.6, 126.3, 122.2, 120.9, 116.9, 114.2, 69.7, 69.1, 32.2, 30.0–29.8, 29.7–29.4, 26.3, 26.2, 22.9, 14.4.