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Supporting Information

Photoinduced Electron Transfer and Photovoltaic Devices of a Conjugated Polymer with Pendant Fullerenes

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The convergent synthetic route towards the monomer 1 (=S10b) is shown in Scheme 1. Commercially available catechol (S1) was bis-alkylated with n-hexyl bromide yielding S2 (neat, 91 %). Subsequently, Friedel-Crafts acylation with 5-bromopentanoyl chloride afforded S3 in 88 % as the first building block. Synthesis of the second building block (S7) started from commercial hydroquinone dimethyl ether (S4). para-Bis-iodination was followed by demethylation using boron tribromide, yielding S6 following literature procedures. Subsequent alkylation with 1.0 equivalent n-hexyl bromide in an ethanol/water mixture yielded monoalkylated diiodohydroquinone S7 in 27 %. Ketone S8 was obtained by a Williamson etherification reaction between building blocks S3 and S7 in 93 % yield. Subsequently, reaction with p-tosyl hydrazide yielded the corresponding tosyl hydrazone S9, which was purified by column chromatography (silica gel; chloroform) yielding pure compound S9 (95 %).

Monomer (S10) was subsequently prepared using the following procedure: First, heating the anion of S9 in the presence of [60]fullerene in 1,2-ortho-dichlorobenzene (ODCB) at 80-90 ºC gave fulleroid S10a, together with methanofullerene S10b, higher adducts and [60]fullerene. After column chromatography, the obtained mixture of S10a and S10b in ODCB was photoisomerized quantitatively to S10b. Final purification was done by column chromatography, affording pure S10b as a brown powder in 37 % (4 steps, starting from S9).

S10b showed 30 signals for C60-sp2 carbons in 13C NMR, a number allowing for Cs symmetry (maximum 31 sp2-carbon resonances). The resonances at δ 87.21 and 87.16 are
indicative for iodo-substituted benzene rings and the resonances at $\delta$ 80.24 and 52.17 are characteristic for the cyclopropyl moiety. In UV-Vis, $\textbf{S10b}$ shows characteristic absorptions for a methanofullerene [330 nm ($\epsilon$ = 44100), 433 nm (2870), 496 nm (1790), and 699 nm (272)], and also the FTIR-spectrum was in accordance with the proposed structure (ArOR (1209 and 1052 cm$^{-1}$), fullerene (526 cm$^{-1}$)). The MALDI-TOF spectrum of $\textbf{S10b}$ featured a parent peak at $m/z$ = 1510.6.

**Scheme 1.** Synthesis of $\textbf{S10b}$ a. 1. KOH, neat; 2. n-HexBr, 60 °C, 3 h., 91 %; b. Br(CH$_2$)$_4$COCl, AlCl$_3$, CH$_2$Cl$_2$, 0 °C, 88 %; c. I$_2$, KIO$_3$, HOAc, H$_2$SO$_4$, H$_2$O, $\Delta$, 6h., 71 %; d. BBr$_3$, CH$_2$Cl$_2$, -78 °C, 87 %; e. n-HexBr, KOH, EtOH, H$_2$O, 27 %; f. $\textbf{S3}$, K$_2$CO$_3$, MIBK, $\Delta$, 16h., 93 %; g. TosNHNH$_2$, EtOH, $\Delta$, 3 h., 95 %; h. 1. NaOMe, py, 2. [60]fullerene, 65 °C, 16 h., 3. $\nu$, ODCB, 500 W flood lamp, 2.5 h., 37 % (4 steps).

Diethynylene monomer 2 (=S21) was readily synthesized starting from methylhydroquinone ($\textbf{S11}$) (Scheme 2). Etherification of $\textbf{S11}$ with 2-ethylhexyl-p-toluenesulfonate, followed by radical bromination using NBS in the presence of AIBN and ionic bromination with NBS, gave $\textbf{S13}$. Phosphonate $\textbf{S14}$ was obtained by treatment of $\textbf{S13}$ with triethylphosphite. For the central unit of $\textbf{S21}$ etherification of 4-
methoxyphenol with 3,7-dimethyloctyl-p-toluenesulfonate gave S16, which was then brominated to give S17, followed by bis-formylation using butyllithium and N,N-dimethylformamide to yield dialdehyde S18. A double Wittig Horner coupling of S14 and S18 gave S19 which was reacted with (trimethylsilyl)acetylene using a palladium-catalyzed coupling to afford S21 after deprotection.

Scheme 2. i. \( \text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OTs}, \text{K}_2\text{CO}_3, \text{TBAC, MEK}, 93\% \); j. 1. NBS, AIBN, CCl\(_4\); 2. NBS, THF, 24\%; k. \( \text{P(OEt)}_3, 160^\circ \text{C}, 1.5 \text{ h.} 100\% \); l. \( \text{(CH}_3)_2\text{CH(CH}_2)_3\text{CH(CH}_3)\text{CH}_2\text{CH}_2\text{OTs} \); m. Br\(_2\), HOAc, 65-116 \(^\circ\)C, 2 h. 75\%; n. 1. BuLi Et\(_2\)O; 2. DMF, Et\(_2\)O, -10 \(^\circ\)C, 56\%; o. S14, KtBuO, DMF, 35\%; p. TMS-CCH, NEt\(_3\), PdCl\(_2\), PPh\(_3\), Cu(OAc)\(_2\), 50\%; q. TBAF, THF, 100\%
Experimental Section:

**General remarks pertaining to synthesis and characterization in Groningen.**

All reagents and solvents were used as received or purified using standard procedures. Fullerene (99.5%) was purchased from Bucky USA and used without purification. All reactions were performed under a nitrogen atmosphere unless indicated otherwise. Nitrogen was deoxygenated using a copper column. Flash chromatography was performed using Kieselgel Merck Type 9385 (230-400 mesh). Analytical thin layer chromatography (TLC) was performed using aluminium coated Merck Kieselgel 60 F_{254} plates. Melting points were determined with a Mettler FP1 melting point apparatus equipped with a Mettler FP2 microscope. \(^{1}\)H-NMR and \(^{13}\)C-NMR spectroscopy was performed on a Varian Unity Plus (500 MHz) instrument or on a Varian VXR-300 (300 MHz) instrument at 298 K as indicated. Spectra recorded in CS\(_{2}\) employed a D\(_2\)O insert as external lock and \(^{1}\)H reference (\(\delta = 4.67\) ppm relative to the TMS scale) and CS\(_{2}\) as internal \(^{13}\)C reference (\(\delta = 192.3\) ppm relative to the TMS scale). Coupling constants (\(J\)) are denoted in Hz. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, p = pentet, dd = double doublet, m = multiplet, br = broad. FT-IR spectra were recorded on a Mattson Galaxy 4020 instrument. UV-Vis spectra were recorded on a Hewlett Packard HP 8452 UV-Vis spectrophotometer. MALDI-TOF-MS measurements were performed on a Micromass TofSpec E\textsuperscript{®} apparatus (positive-ion reflectron mode) by using elemental sulphur as a matrix (See: Brune, D. C. *Rapid Commun. Mass Spectrom.* 1999, 13, 384-389). Measurements were performed on 1/1 (v/v) aliquots of the analyte (1 mg/mL in CS\(_{2}\)) and the matrix (elemental sulphur: 20 mg/mL). HPLC analyses were performed on a Hewlett Packard HP LC-Chemstation 3D (HP 1100 Series) using an analytical Cosmosil Buckyprep\textsuperscript{®} column (4.6 x 250 mm). Elemental analyses were performed by the Microanalytical Department of this laboratory.

**General remarks pertaining to synthesis and characterization in Eindhoven.**

All reagents and solvents were used as received or purified using standard procedures. NMR spectra were recorded on a Bruker AM-400 spectrometer at frequencies of 400 and 100 MHz for \(^{1}\)H and \(^{13}\)C nuclei, respectively, or on a Varian Gemini spectrometer at frequencies of 300 and 75 MHz for \(^{1}\)H and \(^{13}\)C nuclei, respectively. Tetramethyilsilane
(TMS) was used as an internal standard for $^1$H NMR and CDCl$_3$ or CS$_2$ for $^{13}$C NMR. Elemental analyses were preformed on a Perkin Elmer 2400 series II CHN Analyzer. Gas chromatography/mass spectrometry (GC-MS) analyses were performed on a Shimadzu GCMS-QP5000 equipped with a WCOT fused silica column (length = 15 m, ID = 0.25 mm). Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed on a Perseptive DE PRO Voyager MALDI-TOF mass spectrometer using a dithranol matrix. A Shimadzu LC-10AT system combined with a Polymer Laboratories MIXED-D column (Particle size: 5µm; Length/I.D. (mm):300 x 7.5) and UV detection (470 nm) was employed for size exclusion chromatography (SEC), using CHCl$_3$ as an eluent (1 ml/min).

**Synthesis of 1-(3,4-dihexyloxyphenyl)-4-bromo-pentan-1-one (S3).** 5-Bromo-pentanoyl chloride (11.97 g, 60 mmol) was dissolved in CS$_2$ (75 mL). Aluminium trichloride (8.91 g, 67.2 mmol) was added in portions at 0 ºC. Subsequently, 1,2-dihexyloxybenzene (S2) (18.69 g, 67.2 mmol) in CS$_2$ (75 mL) was added. The reaction was allowed to stir until the end of visible gas evolution (± 45 min.). Subsequently, the reaction mixture was stirred for another 20 min. at 40 ºC. The reaction mixture turned reddish brown. Cooling to room temperature was followed by removal of the solvent in vacuo. The product was purified by repetitive column chromatography (silica gel; toluene : cyclohexane = 1 : 1) giving 23.31 g (53 mmol, 88 %) pure product 7; m.p.: 53.9 – 54.4 ºC; $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.57 – 7.52 (m, 3H), 6.87 (d, $J = 8.4$, 1H), 4.09 – 4.03 (m, 4H), 3.46 (t, $J = 6.5$, 2H), 2.96 (t, $J = 6.9$, 2H), 2.02 – 1.79 (m, 8H), 1.51 – 1.44 (m, 4H), 1.40 – 1.29 (m, 8H), 0.91 (t, $J = 6.9$, 6H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 198.30, 153.52, 148.89, 129.84, 122.58, 112.41, 111.60, 69.25, 69.04, 36.91, 33.37, 32.27, 31.54, 31.51, 29.11, 28.98, 25.65, 25.62, 23.13, 22.56, 13.98; FTIR (KBr): 1665 (s); HRMS Calcd for $^{12}$C$_{23}$H$_{37}$BrO$_3$ (M$^+$): $m/z = 440.1922$. Found: $m/z = 440.1927$; Anal. Calcd for C$_{23}$H$_{37}$BrO$_3$: C, 62.58; H, 8.45; Br, 18.10; Found: C, 62.50; H, 8.49; Br, 18.21.

**Synthesis of 1,4-diiodo-2,5-dimethoxy-benzene (S5).** 1,4-Dimethoxybenzene (13.32 g, 96.5 mmol), potassium periodate (8.23 g, 38.5 mmol) and iodine (27.0 g, 106 mmol) were dissolved in a mixture of acetic acid (600 mL), water (60 mL) and sulphuric acid (6 mL). The reaction mixture was heated under reflux for 6 h. After cooling to room temperature aqueous sodium dithionite (20 %) was added until the excess of iodine was
removed. The formed precipitate was filtered, washed with ethanol, dried \textit{in vacuo} and crystallised from a mixture of methanol and chloroform yielding 20.96 g (53.7 mmol, 56 %) pure S5. A second crop was obtained from the mother liquor (5.69 g, 14.6 mmol, 15 %). Combined yield: 26.65 g (68.3 mmol, 71 %); m.p.: 171.6 – 172.3 °C; $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.19 (s, 2H), 3.83 (s, 6H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 153.26, 121.56, 85.43, 57.14; FTIR (KBr): 1063 (s), 1017 (s); HRMS calcd for C$_8$H$_8$I$_2$O$_2$ 389.8614, found 389.8610.

**Synthesis of 2,5-diiodo-1,4-dihydroxybenzene (S6).** 2,5-Diiodo-1,4-dimethoxybenzene (S5, 22.0 g, 56.6 mmol) was dissolved in dichloromethane (150 mL) and cooled to -78 °C. Boron tribromide (60 g), dissolved in dichloromethane (45 mL), was added dropwise. The resulting solution was allowed to reach room temperature while stirring overnight. The resulting reaction mixture was poured on ice and the obtained solid filtered. The residue was dried \textit{in vacuo}. Final purification was done by crystallisation from THF/cyclohexane giving 17.70 g (48.9 mmol, 87 %) pure product S6; m.p.: 194.1 – 195.5 °C; $^1$H NMR (DMSO, 300 MHz): $\delta$ 9.78 (br s, 2H), 7.14 (s, 2H); $^{13}$C NMR (DMSO, 75 MHz): $\delta$ 150.36, 123.55, 84.28; FTIR (KBr): $\approx$ 3242 (m), 1407 (s), 1046 (m); HRMS calcd for C$_6$H$_4$I$_2$O$_2$ 361.830, found 361.831.

**Synthesis of 2,5-diiodo-4-hexyloxyphenol (S7).** 2,5-Diiodo-1,4-dihydroxybenzene (S6, 3.62 g, 10 mmol) was dissolved in ethanol (100 mL), and n-hexyl bromide (1.65 g, 10 mmol) was added. The reaction was heated under reflux. Subsequently, an aqueous solution of KOH (560 mg/10 mL) was added dropwise. The reaction mixture was heated under reflux for 3 h, whereafter the mixture was poured on water, acidified and extracted with dichloromethane (3 x 200 mL). The combined organic layers were dried and evaporated \textit{in vacuo}. The $^1$H NMR showed the presence of mono- and bisalkylated product. These were separated by column chromatography (silica gel; chloroform : cyclohexane = 1 : 1) giving 1,4-dihexyloxy-2,5-diiodobenzene (704 mg, 1.33 mmol, 13 %) and 2,5-diiodo-4-hexyloxyphenol (S7, 1.244 g, 2.74 mmol, 27 %, 54 % of the optimal statistical mixture); m.p.: 58.3 – 59.4 °C; $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.42 (s, 1H), 7.03 (s, 1H), 4.92, (s, 1H), 3.92 (t, $J = 6.3$, 2H), 1.86 – 1.76 (m, 2H), 1.57 –1.43 (m, 2H), 1.38 –1.35 (m, 4H), 0.92 (t, $J = 6.9$, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 152.64, 149.80, 124.79, 120.92, 87.59, 84.35, 70.37, 31.43, 29.05, 25.68, 22.56, 14.01; FTIR (KBr): 3253
HRMS Calcd for $^{12}$C$_{12}$H$_{16}$I$_{2}$O$_{2}$ (M$^+$): m/z = 446.9239. Found: m/z = 446.9240.

**Synthesis of 1-(3,4-bis-hexyloxy-phenyl)-5-(4-hexyloxy-2,5-diiodo-phenoxy)-pentane-1-on (S8).** 2,5-Diiodo-4-hexyloxyphenol (S7, 1.22 g, 2.74 mmol) and 1-(3,4-dihexyloxyphenyl)-4-bromo-pentan-1-one (S3, 1.33 g, 3.02 mmol, 1.1 eq.) were dissolved in methyl-iso-butylketone (100 mL), and potassium carbonate (1.51 g, 10.9 mmol) was added. The solution was heated under reflux for 16 h. Subsequently, the solvent was evaporated in vacuo. The obtained solid was partitioned between dichloromethane (200 mL) and water (200 ml). The aqueous phase was extracted with dichloromethane (3 x 100 mL). The combined organic layers were washed with water and evaporated in vacuo. Repetitive column chromatography (silica gel; tert-butyl methyl ether : cyclohexane = 1 : 9) yielded 2.05 g (2.54 mmol, 93 %) pure S8; m.p.: 61.0 – 62.3 °C; $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.58 (dd, J = 8.4, J = 1.8, 1H), 7.53 (d, J = 1.8, 1H), 7.19 (s, 1H), 7.17 (s, 1H), 6.87 (d, J = 8.4, 1H), 4.09 – 4.03 (m, 4H), 3.99 (t, J = 5.7, 2H), 3.93 (t, J = 6.6, 2H), 3.05 (t, J = 7.1, 2H), 2.01 – 1.76 (m, 10 H), 1.53 – 1.44 (m, 6H), 1.42 – 1.28 (m, 12 H), 0.97 – 0.88 (m, 9H); $^{13}$C NMR (CDCl$_3$, MHz): $\delta$ 198.64, 153.36, 152.90, 152.64, 148.81, 129.91, 122.69, 122.61, 112.38, 111.57, 86.28, 86.19, 70.29, 69.99, 69.19, 68.96, 37.61, 31.51, 31.48, 31.40, 29.08, 29.05, 28.97, 28.71, 25.65, 25.62, 25.59, 22.53, 21.31, 13.97; FTIR (KBr): 1669 (s); MS: Calcd for $^{12}$C$_{35}$H$_{52}$I$_2$O$_5$ (M$^+$): m/z = 806.190. Found: m/z = 806.194; Anal. Calcd for C$_{35}$H$_{52}$I$_2$O$_5$: C, 52.12; H, 6.50; I, 31.47; Found: C, 52.29; H, 6.69; I, 30.91.

**Synthesis of 1-(3,4-bis-hexyloxy-phenyl)-5-(4-hexyloxy-2,5-diiodo-phenoxy)-pentane-1-on para-tosyl hydrazone (S9).** 1-(3,4-Bis-hexyloxy-phenyl)-5-(4-hexyloxy-2,5-diiodo-phenoxy)-pentane-1-on (S8, 1.99 g, 2.46 mmol) and para-tosyl hydrazide (1.40 g, 7.50 mmol, 3.05 eq.) were dissolved in ethanol (50 mL). The resulting mixture was heated under reflux and the reaction was followed by TLC (silica gel, chloroform). After 3 h. the conversion was almost complete. After cooling to room temperature the solvent was evaporated in vacuo. Final purification was enforced by column chromatography (silica gel, chloroform) giving fractions of the different atropoisomers of pure product S9 in varying E/Z ratio’s (total yield 2.28 g, 2.34 mmol, 95 %) as slightly yellow oils; major isomer: $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.04 (br s, 1H), 7.91 (d, J =
8.1, 2H), 7.32 – 7.24 (m, 3H), 7.17 – 7.12 (m, 3H). 6.76 (d, J = 8.4, 1H), 4.04 – 3.85 (m, 8H), 2.67 (t, J = 7.7, 2H), 2.38 (s, 3H), 1.86 – 1.64 (m, 10H), 1.56 – 1.40 (m, 6H), 1.40 – 1.24 (m, 12H), 0.96 – 0.84 (m, 9H); 13C NMR (CDCl₃, 75 MHz): δ 155.93, 153.08, 152.43, 150.70, 143.95, 135.43, 129.89, 129.45, 128.92, 128.16, 122.92, 122.56, 119.65, 112.43, 111.54, 86.34, 86.28, 70.27, 69.72, 69.09, 69.02, 37.61, 31.59, 31.51, 31.41, 29.21, 29.05, 28.87, 28.37, 26.48, 25.73, 25.65, 25.62, 22.96, 22.59, 22.53, 21.57, 13.98; minor isomer: 1H NMR (CDCl₃, 300 MHz): δ 7.79 (d, J = 8.4, 2H), 7.52 (br s, 1H), 7.14 (d, J = 7.2, 2H), 6.88 (d, J = 8.4, 1H), 6.62 (dd, J = 8.0, 2.0, 1H), 6.58 (d, J = 1.5, 1H), 4.01 (t, J = 6.5, 2H), 3.97 – 3.88 (m, 4H), 3.86 (t, J = 5.6, 2H), 2.54 (t, J = 6.8, 2H), 2.42 (s, 3H), 1.87 – 1.75 (m, 6H), 1.75 – 1.62 (m, 4H), 1.58 – 1.42 (m, 6H), 1.42 – 1.26 (m, 12H), 0.96 – 0.88 (m, 9H); 13C NMR (CDCl₃, 75 MHz): δ 157.71, 152.94, 152.60, 150.18, 149.81, 143.81, 135.46, 129.49, 128.17, 127.88, 124.53, 122.67, 119.57, 113.84, 111.85, 86.26, 86.18, 70.30, 69.77, 69.40, 69.14, 37.59, 31.53, 31.40, 29.11, 29.05, 28.37, 25.63, 22.75, 22.54, 21.60, 13.97; FTIR (KBr): 3216 (m), 1598 and 1575 (m).

Synthesis of methanofullerene S10b (Monomer 1). 1-(3,4-bis-hexyloxy-phenyl)-5-(4-hexyloxy-2,5-diiodo-phenoxy)-pentane-1-on para-tosyl hydrazone (S9, 1.14 g, 1.17 mmol) was dissolved in pyridine (40 mL, dry) and sodium methoxide (62.4 mg, 1.16 mmol) was added. The mixture was stirred for 30 minutes at room temperature, after which a solution of [60]fullerene (765 mg, 1.06 mmol) in ortho-dichlorobenzene (ODCB, 110 mL) was added. The resulting mixture was stirred at 80 – 90 ºC for 16 h. Removal of the solvent in vacuo was followed by column chromatography (silica gel, CS₂ (CAUTION! Pour column in toluene and pretreat the column with CS₂, because mixing silica gel and CS₂ directly generates enough heat to ignite the CS₂)) to remove [60]fullerene (316 mg, 0.44 mmol, 41 %) followed by elution with a mixture of toluene and cyclohexane (1 : 7) giving pure product S10 (703 mg, 0.47 mmol, 44 %) as a mixture of fulleroid S10a and methanofullerene S10b. This residue was redissolved in ODCB (200 mL) and irradiated with a 500 W flood lamp. The reaction was followed by HPLC (Cosmosil; toluene : cyclohexane = 1 : 1) until the [5,6]-isomer had disappeared (± 140 minutes). Removal of the solvent in vacuo was followed by column chromatography (silica gel; toluene : cyclohexane = 1 : 4). The obtained solid was precipitated from
ODCB/MeOH and subsequently suspended in methanol, and centrifuged (2 x). Drying overnight at ~ 50 ºC in vacuo, gave pure product S10b (591 mg, (0.39 mmol, 37 % (4 steps)); m.p.: 94.7 – 95.9 ºC; ¹H NMR (CDCl₃, 500 MHz): δ 7.48 (dd, J = 8.0, J = 2.0, 1H), 7.43 (d, J = 2.0, 1H), 7.24 (s, 1H), 7.19 (s, 1H), 7.03 (d, J = 8.5, 1H), 4.14 (t, J = 5.8, 6H), 4.03 (t, J = 6.3, 2H), 3.08 – 3.02 (m, 2H), 2.34 – 2.28 (m, 2H), 2.18-2.13 (m, 2H), 2.02 – 1.90 (m, 6H), 1.71 – 1.62 (m, 6H), 1.58 – 1.49 (m, 12 H), 1.14 – 1.06 (m, 9H); ¹³C NMR (CDCl₃, 125 MHz): δ 152.63, 152.22, 149.15, 148.63, 148.61, 147.77, 145.65, 144.97, 144.94, 144.90, 144.86, 144.79, 144.59, 144.57, 144.42, 144.23, 144.17, 143.85, 143.56, 143.52, 142.87, 142.82, 142.81, 142.79, 142.71, 142.68, 142.03, 141.94, 141.92, 141.91, 140.76, 140.52, 137.76, 137.65, 128.50, 125.01, 122.17, 122.13, 117.61, 112.81, 87.21, 87.16, 80.24, 69.82, 69.24, 69.20, 68.78, 52.17, 34.04, 32.08, 32.05, 31.93, 29.90, 29.66, 29.62, 26.31, 26.22, 24.21, 23.31, 23.28, 14.60; FTIR (KBr): 1209 (s), 1052 (s), 605 (w), 605 (w), 588 (w), 573 (w), 526 (s); UV-Vis (toluene): 330 (ε = 44100), 433 (2870), 485 (1790), 699 (272); MALDI-TOF MS: Calcd for C₉₅H₅₂I₂O₄ (M⁺): m/z = 1510.2. Found: m/z = 1510.6; Anal. Calcd for C₉₅H₅₂I₂O₄: C, 75.50; H, 3.47; I, 16.79; Found: C, 75.40; H, 3.41; I, 16.74.

Synthesis of 1,4-bis(2-ethylhexyloxy)-2-methylbenzene (S12). Under an argon atmosphere methylhydroquinone (10 g, 80.5 mmol), 2-ethylhexyl-p-toluenesulfonate (48 g, 169 mmol) and tetrabutylammonium chloride (2.66 g, 9.6 mmol) were added to a suspension of K₂CO₃ (66.3 g, 480 mmol) in dry 2-butanone (160 mL). The reaction mixture was stirred for 16 h at reflux temperature. After cooling, the suspension was filtered and the solvent was removed in vacuo. The resulting crude product was purified by column chromatography (silica gel, hexane/CHCl₃ 2:1). Evaporation of the solvent yielded 28.3 g (93%) of S12 as a pure colorless oil: ¹H NMR (CDCl₃) δ 6.79 (d, 1H), 6.77 (d, 1H), 6.71 (dd, 1H), 3.83 (m, 4H), 2.25 (s, 3H), 1.7 (m, 2H), 1.48 (m, 12H); ¹³C NMR (CDCl₃) δ 152.95, 151.50, 127.99, 117.62, 111.66, 111.35, 70.94, 70.79, 39.62, 39.45, 30.68, 30.52, 29.11, 29.07, 24.05, 23.83, 23.08, 16.38, 14.09, 11.21, 11.09; GC-MS (Mw = 348.56) m/z = 348 [M⁺].

Synthesis of 1-Bromo-2,5-bis(2-ethylhexyloxy)-4-bromomethylbenzene (S13). Under an argon atmosphere, NBS (6.12 g, 34.4 mmol) and AIBN (1.72 g, 10.3 mmol) were added to a solution of S12 (10 g, 28 mmol) in dry CCl₄ (28 mL). After stirring for
1h under reflux, the reaction mixture was cooled to room temperature. The mixture was filtered and the solvent evaporated. To remove the last traces of AIBN and NBS, hexane was added to the residue, followed by filtration and evaporation of the solvent. Subsequently, dry THF (28 mL) and NBS (6.63 g, 37 mmol) were added and the reaction mixture was stirred at reflux temperature for 1h. After evaporation of the solvent, hexane was added. The solution was filtered and the solvent removed in vacuo. After column chromatography (silica gel, hexane) and evaporation of the solvents, 3.5 g of S13 (24%) was obtained as a colorless oil. ¹H NMR (CDCl₃) δ 7.06 (s, 1H), 6.80 (s, 1H), 4.48 (s, 2H), 3.84 (m, 4H), 1.76 (m, 2H), 1.4 (m, 16H), 0.92 (m, 12H); ¹³C NMR (CDCl₃) δ 151.20, 149.55, 125.87, 116.98, 115.61, 113.15, 72.35, 71.04, 39.50, 30.57, 30.46, 29.05, 23.97, 23.86, 23.01, 14.05, 11.16.

Synthesis of diethyl[2,5-bis(2-ethylhexyloxy)-4-bromo-benzyl]phosphonate (S14). Triethyl phosphite (1.55 g, 9.33 mmol) and S13 (3.15 g, 6.22 mmol) were stirred at 160 °C for 1.5 h. The reaction mixture was cooled to 75 °C and the ethyl bromide, formed during the reaction, and the excess of triethyl phosphite were distilled under reduced pressure. The product S14 was a light yellow oil. Yield 3.30 g (100%). ¹H NMR (CDCl₃) δ 7.02 (d, 1H), 6.86 (d, 1H), 4.03 (m, 4H), 3.79 (m, 4H), 3.16 (d, 2H), 1.70 (m, 2H), 1.36 (m, 22H), 0.90 (m, 12H); ¹³C NMR (CDCl₃) δ 150.94 (d), 149.34 (d), 120.08 (d), 116.55 (d), 116.25 (d), 110.50 (d), 72.17, 71.27, 61.76 (d), 39.39 (d), 30.38 (d), 28.93 (d), 23.74 (d), 22.88, 16.22 (d), 13.91, 11.01.

Synthesis of 1,4-dibromo-2-(3,7-dimethyloctyloxy)-5-methoxybenzene (S17). A solution of Br₂ (11.78 g, 73.74 mmol) in glacial acetic acid (30 mL) was added dropwise to a solution of 1-(3,7-methyloctoxy)-4-methoxybenzene (S16) (10 g, 37.82 mmol) in glacial acetic acid (45 mL) at 65 °C. After stirring during 45 min at 65 °C, the temperature was raised to reflux during 1h. The solution was then cooled to room temperature and subsequently poured on water (560 mL) and made alkaline with 2N NaOH (660 mL). The aqueous phase was extracted with CH₂Cl₂ (3 x 200 mL). The combined organic layers were washed with brine and dried over MgSO₄. The resultant crude product was purified by column chromatography (silica gel, hexane/CHCl₃ 2:1) Evaporation of the solvent yielded 12 g (75%) of S17 as a colorless oil: ¹H NMR (CDCl₃) δ 7.09 (s, 1 2H), 1.52 (m, 1H), 1.32 (m, 2H), 1.68 (m, 4H), 0.94 (d, 3H), 0.87 (d, 6H); ¹³C
NMR (CDCl$_3$) $\delta$ 150.34, 150.09, 118.38, 116.91, 111.11, 110.13, 68.57, 56.90, 39.13, 37.15, 35.97, 29.70, 27.92, 24.61, 22.66, 22.56, 19.64; GC-MS (Mw = 422.20) $m/z$ = 422 [M]$^+$.  

**Synthesis of 2-(3,7-Dimethyloctyloxy)-5-methoxybezene-1,4-dialdehyde (S18).** Dibromide S17 (7 g, 16.58 mmol) was dissolved in dry diethyl ether (135 mL). The solution was cooled to $-10^\circ$C and 1.6 M n-buthyllithium hexane solution (24.87 mL) was added slowly. The reaction mixture was stirred for 5 min., then, the cooling bath was removed and dry DMF (3.23 mL) was added dropwise. The mixture was stirred for another hour at room temperature. After addition of 6 M HCl (30 mL), the organic layer was washed with water (2 x 100 ml) a saturated NaHCO$_3$ solution (100 mL) and again water (100 mL). The organic layer was dried over MgSO$_4$ and the solvent was evaporated. The resultant crude product was purified by column chromatography (silica gel, hexane/toluene 2:1, $R_f$ = 0.2). Evaporation of the solvent yielded 3.02 g (56%) of S18 as a light yellow solid. $^1$H NMR (CDCl$_3$) $\delta$ 10.54 (s, 1H), 10.49 (s, 1H), 7.44 (s, 2H), 4.13 (m, 2H), 3.94 (s, 3H), 1.88 (m, 1H), 1.66 (m, 2H), 1.53 (m, 1H), 1.25 (m, 6H), 0.96 (d, 3H), 0.87 (d, 6H); $^{13}$C NMR (CDCl$_3$) $\delta$ 189.20, 155.47, 155.28, 129.08, 111.70, 110.58, 67.53, 56.10, 39.11, 37.13, 35.89, 29.83, 27.88, 24.60, 22.61, 22.51, 19.57.  

**Synthesis of (E,E)-1,4-bis[4-bromo-2,5-bis(2-ethylhexyloxy)styryl]-2-(3,7-dimethyloctyloxy)-5-methoxybezene (S19).** Phosphonate S14 (1.82 g, 3.23 mmol) was dissolved in dry DMF (10 mL) under an argon atmosphere and 0.43 g (3.9 mmol) of KtBuO were added to the solution. After 15 min, a solution of dialdehyde S18 (0.5 g, 1.56 mmol) in dry DMF (12 mL) was added dropwise and the reaction mixture was stirred for 3 h. The solution was poured on crushed ice and of 6 M HCl (200 mL) was added. The aqueous phase was extracted twice with diethyl ether and the combined organic layers were subsequently washed with 3 M HCl, water, a saturated aqueous solution of Na$_2$CO$_3$ and dried over MgSO$_4$. The solvent was removed in vacuo. Column chromatography (silica gel, hexane/CHCl$_3$ 4:1, $R_f$ = 0.6) and posterior evaporation of the solvent afforded 0.7g (35%) of S19 as a greenish oil: $^1$H NMR (CDCl$_3$) $\delta$ 7.50 (d, 1H), 7.49 (d, 1H), 7.45(d, 1H), 7.44 (d, 1H), 7.18 (s, 2H), 7.17 (s, 2H), 7.10 (s, 1H), 7.10 (s, 1H), 4.10(t, 2H), 3.92 (m, 11H), 1.9-0.8 (m, 79H); $^{13}$C NMR (CDCl$_3$) $\delta$ 151.37, 151.08, 150.98, 150.90, 149.92, 149.88, 127.10, 127.02, 126.90, 126.84, 123.41, 123.35, 123.22,
122.63, 117.55, 117.41, 111.59, 111.08, 110.72, 110.35, 108.45, 72.34, 72.25, 71.79, 71.50, 67.17, 55.91, 39.61, 39.53, 39.21, 37.29, 36.46, 30.72, 30.73, 30.50, 30.21, 29.10, 29.06, 27.92, 24.70, 24.15, 23.89, 23.87, 23.05, 22.63, 22.54, 19.88, 14.11, 14.08, 14.06, 11.32, 11.26, 11.23, 11.20; MALDI-TOF MS (Mw = 1139.32) m/z = 1138.59 [M]+.

Synthesis of (E,E)-1,4-bis[4-(trimethylsilyl)ethynyl-2,5-bis(2-ethylhexyloxy)styryl]-2-(3,7-dimethyloctyloxy)-5-methoxybezene (S20). (Trimethylsilyl)acetylene (0.114 g, 1.17 mmol) and dibromide S19 (0.5 g, 0.39 mmol) were dissolved in anhydrous triethylamine (8 mL). Argon was purged through the solution for 15 min and the temperature was raised to 80 °C. Then PdCl₂ (6.98 mg, 0.04 mmol), triphenylphosphine (31 mg, 0.11 mmol) and copper(II) acetate (7.8 mg, 0.04 mmol) were added to the solution. The reaction mixture was stirred for 16 h. The solvent was removed in vacuo, the crude solid was dissolved in diethyl ether. The organic layer was washed with a saturated aqueous solution of NH₄Cl and brine. After the organic layer was dried over MgSO₄, the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, hexane/CHCl₃ 85:15, Rₕ = 0.4) and recrystallization from ethanol yielded 230 mg (50%) of S19 as yellow crystals: ¹H NMR (CDCl₃) δ 7.48 (s, 2H), 7.47 (s, 2H), 7.15 (s, 2H), 7.11 (s, 1H), 7.10 (s, 1H), 6.94 (s, 2H), 4.07 (t, 2H), 3.90 (m, 11H), 1.89 (m, 1H), 1.77 (m, 5H), 1.51 (m, 16), 1.34 (m, 20H), 1.14 (m, 4H), 0.92 (m, 33H), 0.26 (s, 18H); ¹³C NMR (CDCl₃) δ 154.90, 151.49, 151.01, 150.40, 150.29, 128.72, 128.58, 127.26, 127.06, 123.94, 123.84, 123.48, 122.83, 117.07, 116.93, 112.17, 110.47, 110.05, 109.62, 108.47, 101.84, 98.86, 71.81, 71.70, 71.64, 71.35, 67.80, 55.94, 39.73, 39.94, 39.63, 39.24, 37.30, 36.47, 30.79, 30.76, 30.54, 30.24, 29.19, 29.15, 27.93, 24.69, 24.21, 23.92, 23.91, 23.09, 23.07, 22.64, 22.55, 19.90, 14.12, 14.08, 14.06, 11.35, 11.32, 11.28, 0.02; MALDI-TOF MS (Mw = 1173.94) m/z = 1173.84 [M]+; Anal. Cald for C₇₅H₁₂₀O₆Si₂: C, 76.7; H, 10.3. Found: C, 76.64; H, 10.33.

Synthesis of (E,E)-1,4-bis[4-ethynyl-2,5-bis(2-ethylhexyloxy)styryl]-2-(3,7-dimethyloctyloxy)-5-methoxybezene (S21). To a solution of S20 (27 mg, 0.02 mmol) in dry THF was added 1 M tetrabuthylammonium fluoride in THF (0.023 mL). The reaction mixture was stirred for 1 min and subsequently filtrated over silica gel using chloroform as eluent. The solvent was removed in vacuo yielding 22.6 mg (100%) of a yellow solid
which was used without further purification: $^1$H NMR (CDCl$_3$) $\delta$ 7.49 (s, 1H), 7.49 (s, 1H), 7.48 (s, 2H), 7.15 (s, 2H), 7.14 (s, 1H), 7.13 (s, 1H), 6.97 (s, 1H), 6.97 (s, 1H), 4.08 (t, 2H), 3.90 (m, 11H), 3.29 (s, 2H), 0.91 (m, 33H); $^{13}$C NMR (CDCl$_3$) $\delta$ 154.87, 151.46, 150.99, 150.39, 150.28, 128.97, 128.81, 127.18, 127.01, 124.11, 124.03, 123.33, 122.73, 117.43, 117.27, 111.13, 110.38, 110.28, 109.88, 108.47, 81.41, 80.53, 80.50, 72.15, 72.05, 71.62, 71.34, 67.73, 55.93, 39.63, 38.57, 39.43, 39.22, 37.29, 36.45, 30.93, 30.76, 30.74, 30.52, 30.22, 29.68, 29.10, 29.06, 27.92, 24.69, 24.18, 23.89, 23.87, 23.05, 22.64, 22.54, 19.88, 14.10, 14.06, 11.31, 11.26, 11.23, 11.20. MALDI-TOF MS (Mw =1029.58) $m/z$ = 1029.45 [M]$^+$. 

**Synthesis of reference polymer (5).** To a sealed tube fitted with a magnetic stirrer was added diiodo monomer 4$^6$ (14.85 mg, 0.025 mmol), diethylnyl monomer 2 (S21) (25 mg, 0.024 mmol), Pd(PPh$_3$)$_4$ (1.16 mg, 0.001 mmol), CuI (0.19 mg, 0.001 mmol), dry Et$_3$N (0.3 mL) and dry orthodichlorobenzene (0.7 mL). The reaction mixture was degassed using freeze-pump-thaw cycles and heated at 75 °C under Ar atmosphere for 24 h. After cooling it to room temperature, the reaction mixture was added dropwise to rapidly stirred EtOH (30 mL). After stirring for 2 h, the precipitate was collected and dried under vacuum overnight. Polymer 5 was obtained as 25 mg (75%) of an orange solid.

**Synthesis of Polymer 3.** This polymer was prepared by a procedure identical polymer 5 using diethylnyl monomer 2 (S21) (22 mg, 0.02 mmol), diiodo monomer 1 (S10b) (27mg, 0.018mmol), Pd(PPh$_3$)$_4$ (0.92 mg, 0.0008 mmol), CuI (0.15 mg, 0.0008mmol), dry Et$_3$N (0.3 mL) and dry orthodichlorobenzene (0.7 mL ). Polymer 3 was obtained as 34 mg (76%) of a brown solid.
$^1$H and $^{13}$C NMR of monomer 1 (S10b)
Maldi spectrum (S₈) of monomer 1 (S₁₀b)

**Photoinduced absorption.** PIA measurements were performed between 0.25 eV and 3.0 eV by exciting thin films on quartz with a mechanically modulated (275 Hz, 25 mW 2 mm diameter, 488 nm) beam from a continuous wave argon ion laser (Spectra physics 2025). The change in transmission of probe light ($\Delta T$) was monitored with a phase-sensitive lock-in amplifier using Si, InGaAs, and cooled InSb detectors after dispersion by a triple grating monochromator. The photoinduced absorption, $-\Delta T/T \equiv \Delta \alpha d$, is directly calculated from the change in transmission after correction for fluorescence, which is recorded in a separate experiment. The lifetime of the photoexcitations has been determined by recording the intensity of the PIA bands as a function of the modulation frequency ($\omega$) in the range of 30-4000 Hz.

**Photovoltaic cells.** For photovoltaic cells, polyethylenedioxythiophene polystyrenesulfonate (PEDOT:PSS, Bayer AG) (90 nm) was spin coated on UV-ozone cleaned glass substrates covered with indium tin oxide (ITO) (140 nm), followed by spin coating a solution of 3 in chloroform to form the active layer of 30 nm as determined
with a Tencor P-10 surface profiler. Finally, an aluminum back electrode (100 nm) was deposited in vacuum to give an active area of 4 mm$^2$. $I/V$ characteristics were measured under ~88 mW/cm$^2$ white-light illumination from a tungsten-halogen lamp filtered by Schott KG1 and GG 385 filters with a Keithley 2400 Source Meter in inert nitrogen atmosphere at room temperature. Surface roughness was determined by AFM.

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