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Harnessing "Click"-Type Chemistry for the Preparation of Novel Electronic Materials

*Michal Firstenberg, Kammasandra Nanjunda Shivananda, Irit Cohen, Olga Solomeshch, Vladislav Medvedev, Nir Tessler, and Yoav Eichen**

Sequence-independent or "click"-type chemistry is applied for the preparation of novel π-conjugated oligomers. A variety of bi-functional monomers for Wittig–Horner olefination are developed and applied in a sequential protection–deprotection process for the preparation of structurally similar π-conjugated oligomers. Selected oligomers are incorporated as the organic semiconductors in light-emitting diodes and a field-effect transistor, demonstrating the potential of the approach.

1. Introduction

A major obstacle for the full realization of the potential embedded in organic optoelectronics and molecular nanoelectronics is the difficulty in assembling by design (i.e., engineering) complicated structures with molecular, electronic grade, precision.[1] In the biology, one finds two sequence-independent synthesis approaches that by far exceed the human capabilities in forming complex materials.

Most of the biological chemical entities are prepared by a target-specific machinery that is tailored to produce one material or a very narrow set of structurally similar compounds. This approach is being utilized in most cases where high fidelity in synthesis is required, as is the case in the biosynthesis of most small molecules. On the other hand, when versatility is the goal, nature adopts a Lego-like sequence-independent synthesis approach.[2] In these cases, nature's machinery produces large numbers of materials that differ in structure and properties out of a very limited number of small building blocks. This approach is being used for the synthesis of oligo- and polynucleic acids, where the sequence of the monomers in the polymer represents the genetic code, and for making peptides, where the sequence of the monomers in the polypeptide chains defines their functionality. Due to the importance of these two reactions to molecular biology, two families of most powerful in vitro syntheses were developed for the preparation of peptide and nucleic acid sequences, both in solutions and on solid supports.[3]

The analogous organic synthesis approach is often referred to as "click" chemistry. Recently, it has been applied to the preparation of π-conjugated materials. Yu presented a stepwise reaction of oligo(*p*-phenylene-vinylene) species with two different monomers, using alternating Heck and Horner–Wadsworth–Emmons (HWE) reactions.[4] Following a similar approach, Tour prepared a large library of phenylene vinylene derivatives.[5] A stepwise HWE protection-deprotection process was utilized by Nierengarten,[6] to synthesize new dumbbell-shaped bis (pyrazolino- [60] fullerene) – oligo phenylene vinylene derivatives, and by Krebs,[7] to prepare oligo phenylene vinylenes for solar cells. Suginome[8] used a protection-deprotection version of the Suzuki-Miyora coupling reaction to make oligoarenes. Bauerle *et al.*[9] used combinatorial parallel synthesis and constructed a library of 16 and then 256 tetramers, as candidates for a liquid crystals device. A combinatorial synthesis on solid support was used by Baurele[10] and Anderson[11] to make oligothiophene library and phenylene-ethynylene pentamers library, respectively, both showing optoelectronic characteristics. Young and Moore[12] have utilized the same method to prepare oligo(1,3-phenylene ethynylene). Recently we have reported on the solution synthesis of oligo homo- and hetero- π-conjugated peptides and their optical and electrical properties.[13]

Here, we apply a Lego-like sequence independent bio-inspired procedure of double-bond formation to produce structurally controlled functional oligomers. We report on the preparation of novel electrically active oligomers using a two step Wittig and Wittig–Horner procedure for making oligo arylene vinylene systems. By fabricating an organic light-emitting diode and a field-effect transistor of these oligomers, we demonstrate the potential embedded in this approach.

The general protection-deprotection Horner–Wadsworth–Emmons (HWE) process using bi-functional monomers is outlined in **Scheme 1**. A monofunctional end group, is used for the first coupling step with a bi-functional monomer, having one of its functionalities (an aldehyde in the present case) protected. The next step is the deprotection of the protected aldehyde of the dimer. This sequence may be repeated several times, using

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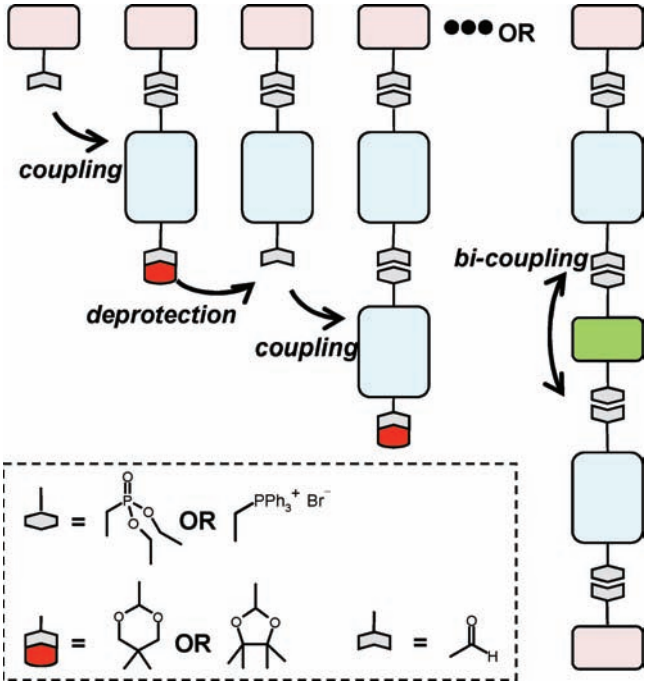


Scheme 1. Schematic illustration of the uni- and bi-directional "click" concept.

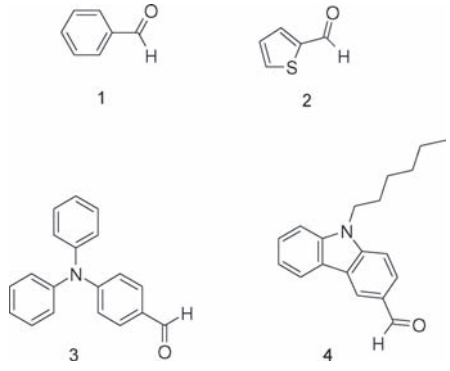
different bi-functional monomers to construct the oligomer with the desired sequence.

2. Results and Discussions

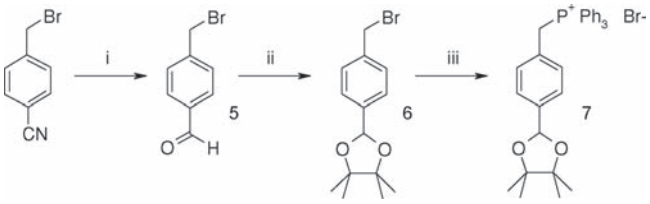
2.1. Monomers

Benzaldehyde, **1**, thiophene-2-carbaldehyde, **2**, 4-diphenylamino-benzaldehyde,[14] **3**, and 9-hexyl-9H-carbazole-3-carbaldehyde, **4**, presented in **Scheme 2**, were used as the start units for the uni-directional process. **Schemes 3–6** present the synthetic routes to bi-functional monomers **7**, **12**, **16**, and **19**, respectively.

4-(4,4,5,5-Tetramethyl-[1,3]dioxolan-2-yl)-benzyl-tripenyl phosphonium bromide, **7**, was produced by converting 4-bromomethyl-benzonitrile[15] to the aldehyde in 88% yield.



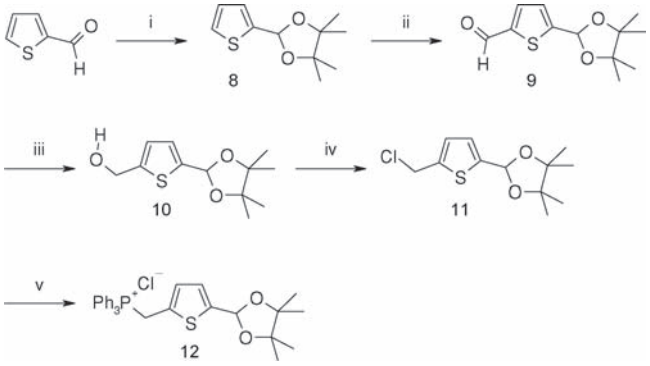
Scheme 2. Start units **1**, **2**, **3**, and **4** of the unidirectional process.



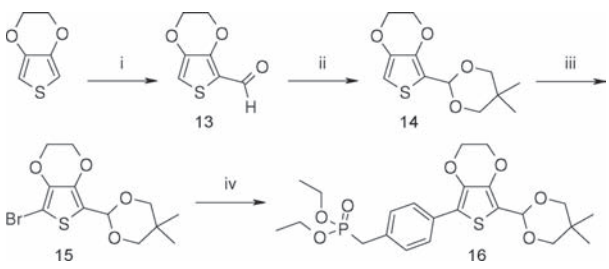
Scheme 3. Synthetic route to **7**, i) DIBAL-H, tetrahydrofuran (THF), 0 °C, 88% yield; ii) 2,3-dimethyl-butane-2,3-diol + H^+, benzene, reflux, 60% yield; iii) Ph_3P, THF, reflux, 93% yield.

Aldehyde **5** was then protected by reacting it with 2,3-dimethyl-butane-2,3-diol under acidic conditions, yielding the acetal **6** (60% yield). **6** was then converted to the phosphonium **7** using a Michaelis–Arbuzov reaction in 93% yield.

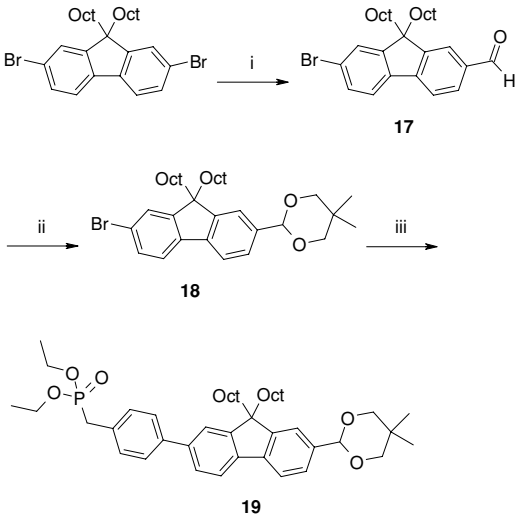
5-(4,4,5,5-Tetramethyl-[1,3]dioxolan-2-yl)thiophen-2-ylmethyl-triphenyl-phosphonium-chloride, **12**, was produced by protecting 2-thiophen-aldehyde with 2,3-dimethyl-butane-2,3-diol under acidic conditions, yielding the acetal **8**. Lithiation of **8** with n-butyllithium followed by a quenching with dry dimethyl-formamide (DMF) gave aldehyde **9**. Reduction of **9** with $NaBH_4$ afforded the alcohol, **10**. Substitution reaction with thionyl chloride yielded **11** and reaction with triphenylphosphine afforded **12** in 47% yield.



Scheme 4. Synthetic route to **12**, i) 2,3-dimethyl-butane-2,3-diol + H^+, benzene, reflux, 90% yield; ii) a: n-butyllithium, b: dimethylformamide (DMF), THF, 0 °C to room temperature (rt), 66% yield; iii) $NaBH_4$, THF, rt, 64% yield; iv) $SOCl_2$, reflux, 53% yield; v) Ph_3P, THF, reflux, 47% yield.



Scheme 5. Synthetic route to **16**, i) $POCl_3$/DMF, −10 °C to rt, quantitative yield; ii) 2,2-dimethyl-propane-1,3-diol + H^+, toluene, reflux, 70% yield; iii) *N*-bromosuccinimide (NBS), acetonitrile, −78 °C to rt, quantitative yield; iv) (4-boronic acid-benzyl)-phosphonic acid diethyl ester,[16] Na_2CO_3, $(Ph_3P)_2PdCl_2$, toluene/water, 100 °C, 45% yield.



Scheme 6. Synthetic route to **19**, i) a: n-butyllithium, b: DMF, THF, −78 °C to rt, 33% yield; ii) 2,2-dimethyl-propane-1,3-diol + H^+, toluene, reflux, quantitative yield; iii) (4-boronic acid-benzyl)-phosphonic acid diethyl ester,[16] Na_2CO_3, $(Ph_3P)_2PdCl_2$, toluene/water, 100 °C, 80% yield.

Monomers **16** and **19** consist of two π-conjugated rings, one being a phenyl ring and the other a 2,3-dihydro-thieno[3,4-b][1,4]dioxine and a 9,9-dioctyl-fluorene, in **16** and **19** respectively. **16** was obtained by reacting 2,3-dihydro-thieno [3,4-b][1,4]dioxine, 3,4-ethylenedioxythiophene (EDOT), with $POCl_3$ and DMF to yield aldehyde **13**, which is then protected with 2,2-dimethyl-1,3-propandiol under acidic conditions to afford the acetal **14**. Bromination of **14** with N-bromosuccinimide (NBS) in acetonitrile yielded **15.** $(Ph_3P)_2PdCl_2$ catalyzed Suzuki heterocoupling between **15** and (4-boronic acid – benzyl)-phosphonic acid diethyl ester[16] in the presence of sodium carbonate afforded **16** as a yellow solid in 45% yield.

19 was made by mono lithiation of 2,7-dibromo-9,9-dimethyl-9H-fluorene with n-butyllithium, followed by quenching with dry DMF. The resulting aldehyde, **17**, was protected with 2,2-dimethyl-1,3-propandiol under acidic conditions, affording acetal **18**. $(Ph_3P)_2PdCl_2$ catalyzed Suzuki heterocoupling between **18** and (4-boronic acid – benzyl)-phosphonic acid diethyl ester[16] in the presence of sodium carbonate afforded **19** as colorless oil in 80% yield.

Each of the bi-functional monomers consists of a π-conjugated backbone and bears two functional groups: a phosphine/phosphonate and a protected aldehyde. These monomers are thus suitable for recurrent Wittig/Wittig–Horner reactions, both as the aldehyde and as the phosphine/phosphonate moieties.

2.2. Dimers

The synthesis of a small library of first-generation dimers was achieved by coupling monomers **1** and **2** with the aldehyde protected bi-functional monomers **7** and **12**. All four reactions were performed using the same conditions: ethanol as the solvent, 2 equivalents of sodium ethoxide (with respect to the phosphor derivative) as the base, 1 h at room temperature, **Scheme 7**. NMR spectra taken for the crude clearly show that all the reactions proceeded in a quantitative yields (>98% yield, Z/E (cis/trans) ratio: 2/3, 2/3, 1/3 and 2/3 for **20–23,** respectively).

The second library of dimers consists of Wittig coupling products from aldehydes **3** and **4** with bi-functional monomers **16** and **19**. Here too, all four reactions were performed using the same conditions: tetrahydrofuran (THF) as the solvent, 3 equivalents of t-BuOK as the base, 1 h at room temperature, **Scheme 8**. NMR spectroscopy revealed quantitative yields for all four dimers **E-24** – **E-27** (E isomers).

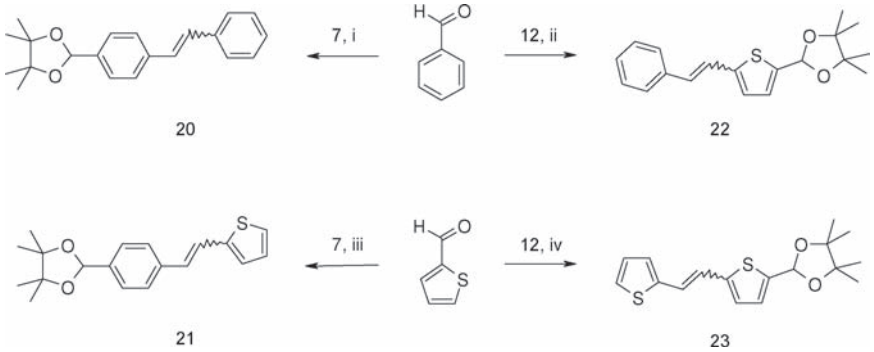
2.3. Trimers and Higher Oligomers

E-dimers **E-20**, **E-21**, and **E-22** were deprotected in an acid catalyzed process, yielding E-dimers **E-28**, **E-29**, and **E-30** in quantitative yields. The deprotected dimers were coupled with a second bi-functional monomer, yielding trimers **E,E-31**, **E,E-32**, and **E,E-33**, **Scheme 9**. All three reactions were performed using the same conditions: deprotection step: 10% HCl in 1:2 water:THF, 3 h, rt. Coupling step: 2 equivalents of sodium ethoxide in ethanol, 1 h, rt. NMR spectra taken for the crude clearly show that all the reactions proceeded in a quantitative yields (>98% yield, predominantly the E,E isomers).

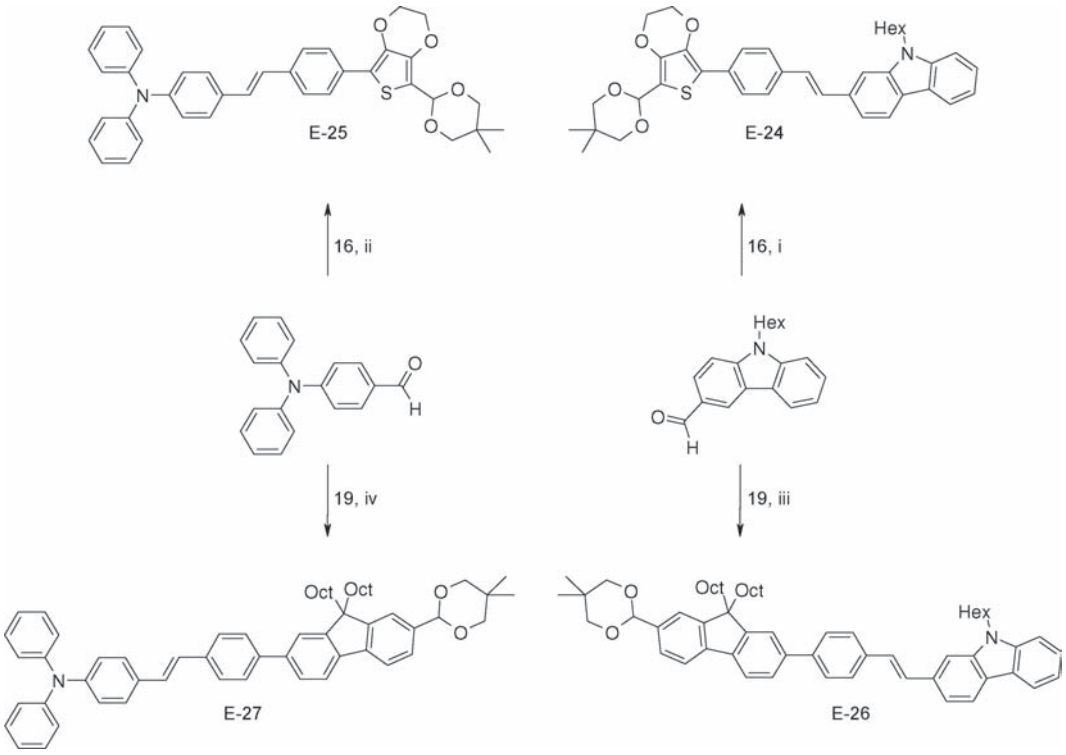
In a similar manner, dimer **E-25** was deprotected using TFA and the resulting aldehyde, **E-34**, was reacted with bi-functional monomer **19** (THF, t-BuOK, 1 h, rt.), yielding trimer **E,E-35**, which was, in turn, deprotected under 5% HCl to yield aldehyde **E,E-36**, **Scheme 10**. In an alternative route, two equivalents of dimer **25** were coupled with the symmetrical bi-functional reagent **37**[17] (THF, t-BuOK, 2 h, 0 °C), forming oligomer **38**, **Scheme 11**.

2.4. Characterization of the New Oligomers

The absorption and emission spectra of **E-20** – **E-27**, **E,E-35**, and **E,E,E,E-38** are depicted in **Figure 1** and **2**. Interestingly, despite the structural similarities, **E-20**, **E-21**, **E-22**, and **E-23**

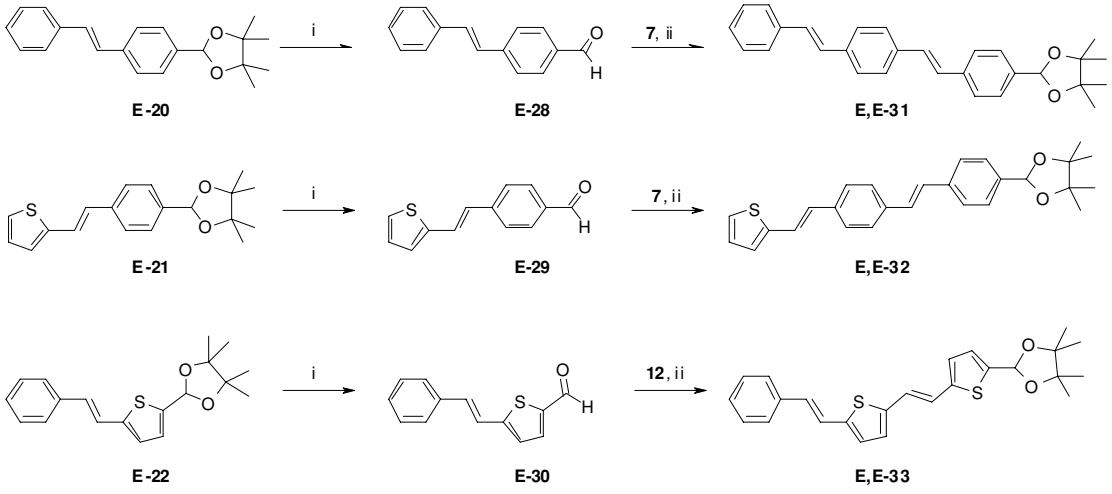


Scheme 7. The synthesis of four first generation arylene-vinylenes dimers (**20**, **21**, **22**, and **23**), made from Wittig coupling of **1** and **2** with bi-functional monomers **7** and **12**. i = ii = iii = iv: ethanol, sodium ethoxide, rt, 1 h, quantitative yields.

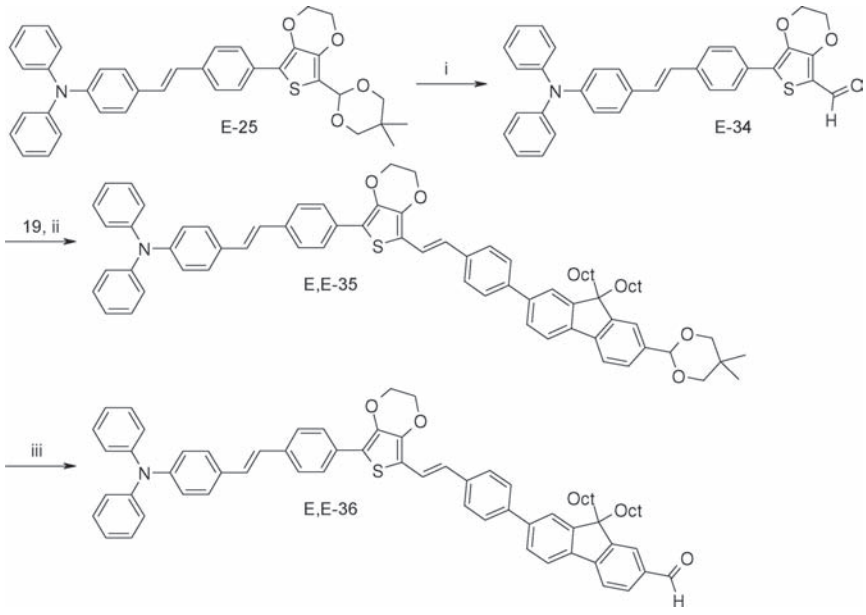


Scheme 8. The synthesis of four first generation arylene-vinylenes dimers (**E-24**, **E-25**, **E-26**, and **E-27**), made from Wittig–Horner coupling of **3** and **4** with bi-functional monomers **16** and **19**. i = ii = iii = iv: THF, t-BuOK, rt, 1 h, quantitative yield).

display different absorption and emission spectra, even in the case of **E-21** vs. **E-22**, where the molecules differ only by the position of the protective group substituent. The electronic levels of the different oligomers were deduced from the absorption edge in their absorption spectra and from their cyclic voltammograms.[18] **Table 1** depicts the resulting highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) values and the optical properties of the different oligomers. **Figure 3** presents the calculated band gap as a function of $1/NDB$, where NDB denotes the number of conjugated double bonds in the systems, a simple measure of the conjugation length, L. Clearly, the band gap of the systems does not obey a simple L^{-1} dependency, as was frequently observed for oligo conjugated systems.[19] Furtheremore, in some subsets of the oligomer family in question, a negative slope is observed. One may attribute this discrepancy to the differences in the contribution of thiophene and phenyl rings to the degree of conjugation,

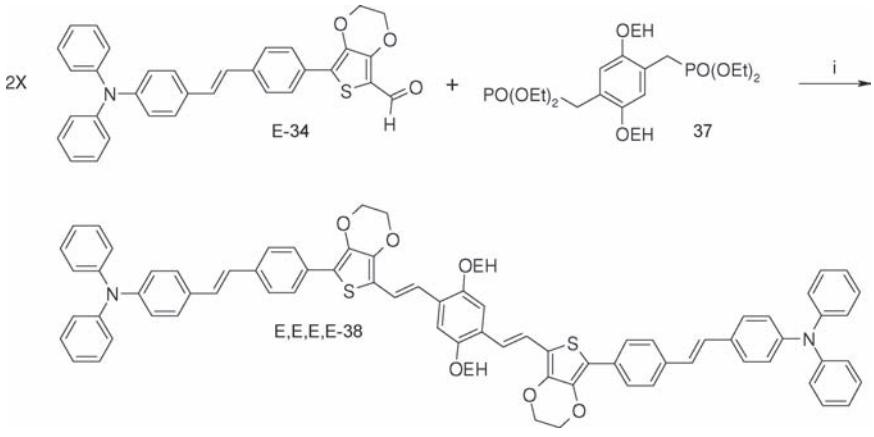


Scheme 9. The synthesis of a partial library of second-generation arylene-vinylenes trimers **E,E-31**, **E,E-32**, and **E,E-33**. i) 10% HCl : THF, 60 °C, 3 h. ii) ethanol, sodium ethoxide, rt, 1 h, quantitative yields.



Scheme 10. Preparation of trimer **E,E-35** and **E,E- 36**. i: TFA. ii: **19**, THF, t-BuOK, 1 h, rt. iii: 5% HCl.

irrespective of their position in the oligomeric structure. This may be related to the improved stability of the quinoid structure of thiophene ring relative to the phenyl ring.[19] Thus, the correlation between the calculated band-gap and conjugation length could be better linearized by applying a different contribution to thiophene and phenyl rings. As evident from Figure 3b, the best-fit to a linear form (yielding the minimal linear-regression residue) is $L_{eff} = NDB + (2 \times NTR)$, where *NTR* denotes the number of thiophene rings. Applying this correction, the spread in all the libraries is much smaller in the corrected graph. The linear fit (dashed line) yields a band gap of 1.7 eV at (1/conjugation)→0, suggesting the minimal band-gap obtainable for this family of mixed thiophene vinylene phenylene systems. The HOMO and LUMO versus the corrected measure of conjugation is given in **Figure 4**.



Scheme 11. Preparation of oligomer **E,E,E,E-38**. i: THF, t-BuOK, 2 h, 0 °C.

2.5. Organic Light-Emitting Diode (OLED)

E,E-35 and **E,E,E,E-38** form good quality and luminescent films when spin-coated from THF solutions. The absorption and emission spectra of films of **E,E-35** and **E,E,E,E-38** were given in Figure 1 and 2. The quantum efficiencies of luminescence of **E,E-35** and **E,E,E,E-38** were 45% (excitation wavelength, λ_{ex} = 370 nm, emission wavelength, λ_{em} = 550 nm) and 17% (λ_{ex} = 500 nm, λ_{em} = 630 nm) respectively.[20]

Both **E,E-35** and **E,E,E,E-38** were incorporated as the emissive layer in a simple light-emitting diode structure consisting of indium tin oxide (ITO), poly(3,4-ethylenedioxythiophene) (PEDOT), the emissive oligomer, Ca, and Al.[21] An ITO-covered glass substrate is spin coated with a 60–70 nm layer of PEDOT and annealed at 110 °C under vacuum. 60–70 nm of the relevant oligomer are subsequently spin coated atop the PEDOT and covered with Ca (30 nm) and Al (120 nm) cathodes.

Figure 5 presents the current and brightness of the OLEDs made of **E,E-35** and **E,E,E,E-38** as a function of the applied bias. The emission of **E,E-35** and **E,E,E,E-38** onsets at about 6.5 V and 3.5 V, respectively. The lower threshold and higher brightness of the **E,E,E,E-38** based LED is directly related to its lower bandgap and the lower barrier to electron injection as its LUMO is closer to the workfunction of Ca. The Commission Internationale de l'Eclairage (CIE) chroma coordinates of the OLEDs were CIE = (*x*,*y*) = (0.3598, 0.5982) and CIE = (*x*,*y*) = (0.6354, 0.3625) for **E,E-35** and **E,E,E,E-38**, respectively.

2.6. Organic Field-Effect Transistors (OFET)

Organic field effect transistors[22,23] were fabricated in a bottom-contacts configuration[24] by spin coating a 40 nm thick film of oligomer **E,E,E,E-38** atop an OFET structure using a previously described procedure.[25] **E,E,E,E-38** functions as the hole conducting channel in the p-type FET, which is switched on at negative gate-source voltages.

Figure 6 depicts the OFET's transfer characteristics, i.e. the drain-source currents (I_{DS}) as a function of gate-source voltage (V_G) for several drain-source voltages (V_{DS} = –2, –7, and –12 V). The logarithmic graph (left) reveals the very low V_G threshold ($V_T \approx 0$). The off current measured at $V_G = 0$ is $I_{DS} \approx 0.1$ nA and is at least an order of magnitude lower at slightly postive gate bias, very low compared to previously published phenyl-thiophene co-oligomers.[26] The

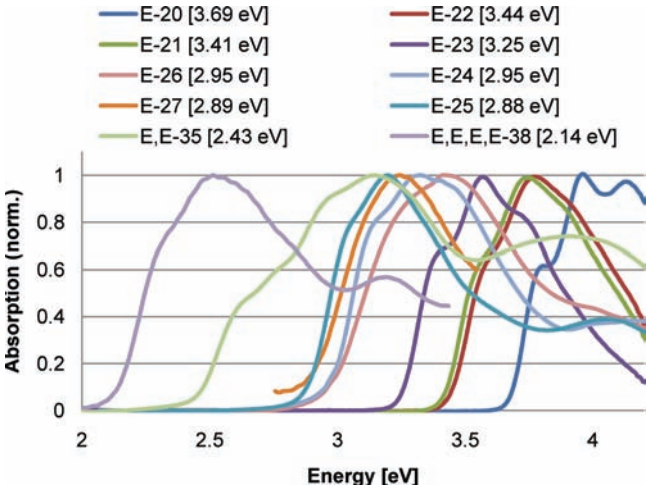


Figure 1. Absorption spectra of conjugated oligomers **E-20** – **E-27**, **E,E-35**, and **E,E,E,E-38**.

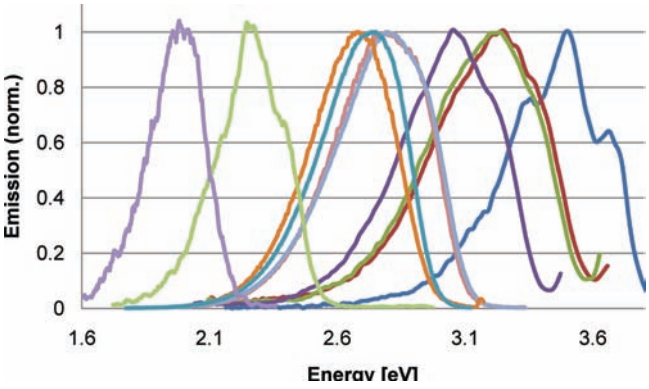


Figure 2. Emission spectra of conjugated oligomers **E-20** – **E-27**, **E,E-35**, and **E,E,E,E-38** (legend as in Figure 1).

linear region at large enough $|V_G|$ is clearly distinguishable. **Figure 7** depicts the current as a function of V_{DS} for different V_G values. The initial linear incline, followed by the quadratic region, is saturated at $V_{DS} = V_G$, as expected [23] when $V_T \approx 0$.

Table 1. Electronic and optical properties of the different oligomers.

Material	HOMO [eV]	LUMO [eV]	Absorption (edge) [eV]	Absorption (max) [eV]	Emission (max) [eV]
E-20	5.6	1.9	3.7	3.8	3.5
E-21	5.4	1.9	3.4	3.5	3.2
E-22	5.3	1.9	3.4	3.5	3.2
E-23	5.3	2.0	3.3	3.4	3.1
E-24			3.0	3.3	2.8
E-25	5.2	2.3	2.9	3.2	2.7
E-26			3.0	3.4	2.8
E-27	5.0	2.1	2.9	3.3	2.7
E,E-35	5.0	2.6	2.4	3.1	2.3
E,E,E,E-38	5.0	2.9	2.1	2.5	2.0

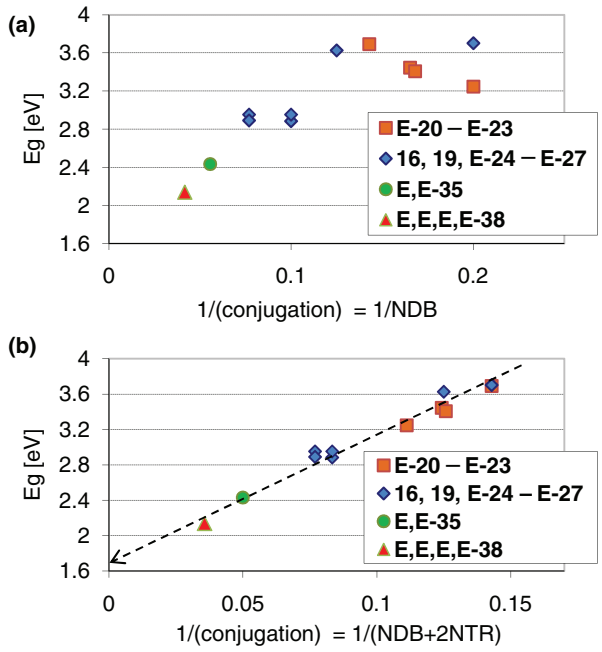


Figure 3. Energy band-gap versus the inverse conjugation for the (**E-20** – **E-23**) library, the (**16**, **19**, **E-24** – **E-27**) library, and the complex oligomers (**E,E-35** and **E,E,E,E-38**): a) without correction and b) with a corrected conjugation measure, incorporating the additional contribution of the thiophene rings.

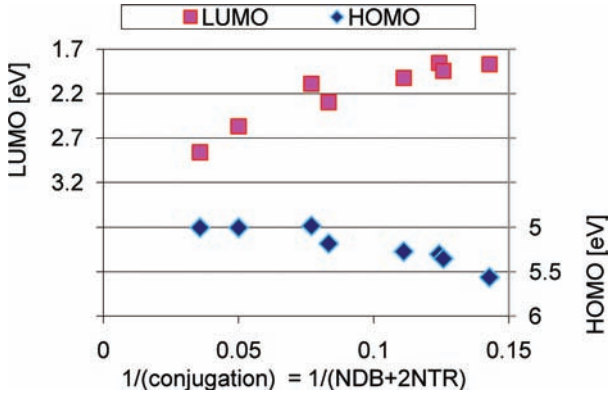


Figure 4. HOMO and LUMO energies as a function of the corrected measure of inverse conjugation.

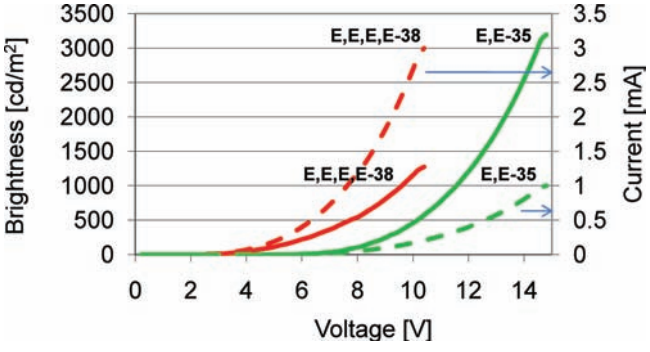


Figure 5. Device performance: brightness (solid lines) and current (dashed) of the three-layer OLED devices, with oligomers **E,E-35** (green) and **E,E,E,E-38** (red).

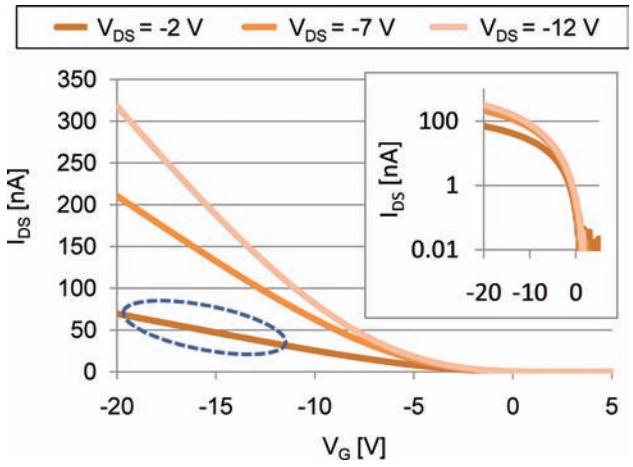


Figure 6. Field effect characteristics of a transistor made of **E,E,E,E-38**. Source-drain current as a function of V_G, for various values of V_{DS}. Inset is in logarithmic scale; the source electrode is set as ground. The blue ellipse marks the "linear region", from which the mobility was calculated.

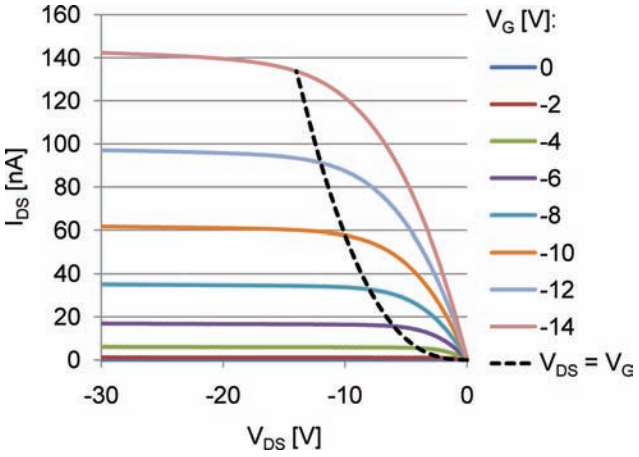


Figure 7. Field effect characteristics of a transistor made of **E,E,E,E-38**. Source-drain current as a function of the drain-source voltage, for various values of the gate-source voltage. The dashed line passes through $V_{DS} = V_G$ points.

As a material characterization, one may extract the charge (holes) mobility of **E,E,E,E-38** from the transfer curves. In the linear region ($V_{DS} << V_G$; blue ellipse in Figure 6), and assuming $V_T \approx 0$, the drain-source current is approximately given by[23]

$$I_{DS} \cong WC_{OX} V_G \times \mu \times \frac{V_{DS}}{L}, \quad (1)$$

where μ is the mobility, W = 11 mm and L = 4 μm are respectively the effective length and separation of the electrodes, and C_{ox} = 40 nF cm^{-2} is gate capacitance per unit of area. For I_{DS} = 70 nA, V_{DS} = 2 V, and V_G = 20 V, we find $\mu = 5 \cdot 10^{-5}$ cm^2 V^{-1} s^{-1}.

3. Conclusions

A series of novel π-conjugated oligomers were prepared in very high yields using a sequence-independent and Lego-like "click" chemistry, based on Wittig and Wittig-Horner protection-deprotection procedures. Tuneability of the optical and HOMO–LUMO band positions was demonstrated, showing the potential in using such an approach. A direct relation between the band gap of the oligomers and their degree of conjugation was demonstrated. The latter is given by the number of double bonds along the molecule backbone, with an additional contribution of two effective bonds for each thiophene ring. Low band gap energies (2.4 eV and 2.15 eV) were deducted for the longest oligomers, only 20–30% higher than the minimal possible band gap determined for this family (1.7 eV). Finally, OLEDs and OFETs were made of selected materials, demonstrating the potential embedded in the "click" chemistry approach.

4. Experimental Section

General: All the starting materials and solvents described in the manuscript were purchased from Sigma-Aldrich and Fluka. Solvents and starting materials were used as received unless noted. Anhydrous solvents were obtained using standard methods.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 792056 – 792064. Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html.

Apparatus: NMR spectra were recorded on Bruker-AM-300 and Bruker-AM-500 spectrometers. Mass spectra were recorded using matrix-assisted laser desorption ionization (MALDI) micro MX (MICROMASS) and TSQ-70B (FINNIGAN MAT). Melting points were recorded on a PL-DSC (Polymer Laboratories) machine. Absorption and emission spectra were recorded on a Shimadzu UV-1601 spectrometer and a Perkin Elmer LS 50 luminescence spectrometer respectively. All optical measurements were performed in analytical grade solvents.

Solution processing and all films and devices were made in a nitrogen glove-box (LABMASTER 130, M. Braun, GmbH, Germany) integrated with a thermal evaporator. PL quantum efficiency measurements were carried out using a IS-040-SL integrating sphere (Labsphere) that was fiber coupled to the FS920 fluorimeter (Edinburgh Instruments) and the procedure was as previously described.[31] The substrates of the FET devices were prepared as described in reference 25. All current–voltage characteristics of OLEDs and FETs were recorded using a 4155B Semiconductor Parameter Analyzer (Agilent).

Materials: *4-bromomethyl-benzaldehyde* (**5**):[15] 34 mL of a 1.5 M solution of diisobutylaluminium hydride, DIBAL-H, in toluene were added to a stirred solution of 5 g (25 mmol) 4-bromomethyl-benzonitrile in 50 mL of dry THF, over a period of 10 min at 0 °C. After stirring for 24 h at 0 °C the solution was diluted with 50 mL of diethyl ether, treated with 100 mL of an aqueous HCl solution (10%) and extracted with diethyl ether. The combined organic extracts were dried over Na_2SO_4 and evaporated. The product was separated over alumina (7:3, hexane:methylene chloride) to give 4.5 g (88% yield) of **5** in the form of a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.99 (s, 1H), 7.85 (d, 2H), 7.52 (d, 2H), 4.48 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 191.6, 136.8, 129.7, 32.1. melting point (mp) = 89 °C. Mass spectrum (MS) (CI+): *m/z*: 199.0 (M^+).

2-(4-bromomethyl-phenyl)-4,4,5,5-tetramethyl-[1,3]dioxolane (**6**):[27] A solution of **5** (4.5 g, 22 mmol), 2,3-dimethyl-butane-2,3-diol (5.3 g, 45 mmol) and a catalytic amount of *p*-toluenesulfonic acid in benzene (100 mL) was refluxed for 72 h. The reaction mixture was then washed with brine, dried over Na_2SO_4 and evaporated. The product was purified over alumina (7:3, hexane:methylene chloride) to give 4.0 g. (60% yield) of **6** in the form of a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.46 (d, 2H), 7.34 (d, 2H), 5.94 (s, 1H), 4.47 (s, 2H), 1.26 (s, 6H), 1.19 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 128.9, 126.5, 99.4, 82.7, 24.2, 22.1. mp = 40 °C. MS (CI+): *m/z*: 299.0 (M^+).

Triphenyl-[4-(4,4,5,5-tetramethyl-[1,3]dioxolan-2-yl)-benzyl] phosphonium bromide (**7**): Triphenyl phosphine (6 g, 26 mmol) was added to a stirred solution of **6** (4 g, 13 mmol) in 15 mL of dry THF and the reaction was refluxed for 72 h under nitrogen. The white precipitate was filtered, washed with several portions of hexane and dried, affording 6.5 g (93% yield) of **7** in the form of a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.74 (m, 9H), 7.61 (m, 6H), 7.25 (d, 2H), 7.06 (d, 2H), 5.85 (s, 1H), 5.42 (s, 1H), 5.37 (s, 1H), 1.26 (s, 6H), 1.19 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 140.2, 140.1, 134.9, 134.4, 134.3, 131.4, 131.3, 130.1,130.0, 126.8, 118.1, 117.4, 99.2, 82.7, 24.2, 22.1. mp > 200 °C. MS (time of flight (TOF) by laser deposition (LD^+)): *m/z*: 481.2 (M^+).

4,4,5,5-Tetramethyl-2-thiophen-2-yl-[1,3]dioxalane (**8**): A solution containing thiophen-2-carbaldehyde (2.8 mL, 30 mmol), 2,3-dimethyl-butane-2,3-diol (7 g, 60 mmol), and a catalytic amount of *p*-toluenesulfonic acid in 100 mL of benzene was refluxed for 72 h. The reaction mixture was then washed with brine, dried and evaporated and the product was isolated using chromatography over alumina (9.5:0.5, hexane:ethyl acetate) yielding 5.7 g (90% yield) of **8** as a pail yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.29 (d, 1H), 7.13 (d, 1H), 6.95 (t, 1H), 6.19 (s, 1H), 1.30 (s, 6H), 1.28 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 143.7, 126.4, 126.0, 96.6, 82.8, 24.2, 22.0. MS (TOF by electron spray (ES+)): *m/z*: 213.19 ($M+H^+$).

5-(4,4,5,5-Tetramethyl-[1,3]dioxalan-2-yl)-thiophen-2-carbaldehyde (**9**): 8 mL (11 mmol) of a n-butyllithium solution (1.6 M in hexane) were added slowly to a solution of **8** (2 g, 9 mmol) in 20 mL of dry THF at 0 °C. The solution was then left to reach room temperature and stirred for additional 5 h. A solution of 3 g ammonium chloride in 50 mL water was added and the mixture stirered for 10 min. The layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure. The product was purified over alumina (8 :2 hexane: ethyl acetate) to give 1.5 g of **9** as a yellow oil (66% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.87 (s, 1H), 7.64 (d, 1H), 7.20 (d, 1H), 6.14 (s, 1H), 1.27 (s, 6H), 1.26 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 183.6, 152.3, 133.5, 133.6, 126.6, 99.4, 65.2, 22.5, 13.9. MS (TOF ES+): *m/z*: 241.32 ($M+H^+$).

[5-(4,4,5,5-Tetramethyl-[1,3]dioxalan-2-yl)-thiophen-2-yl]-methanol (**10**): Sodium borohydride (0.54 g, 14 mmol) was added to a stirred solution of **9** (1.4 g, 6 mmol) in 10 mL THF. The reaction was stirred under nitrogen at room temperature for 30 min then excess sodium borohydride was destroyed by slow addition of acetone (5 mL). The solution was evaporated and the crude was dissolved in ethylacetate. The organic layer was washed with brine, dried over Na_2SO_4 and evaporated under reduced pressure. The product was purified over alumina (6.5:3.5, hexane:ethyl acetate) to give 0.9 g of **10** as a yellow oil (64% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 6.99 (d, 1H), 6.84 (d, 1H), 6.12 (s, 1H), 4.76 (s, 2H), 1.27 (s, 6H), 1.26 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 126.1, 124.8, 96.6, 60.3, 22.0, 14.0. MS (TOF MS AP+): *m/z*: 241.1 ($M-H^+$).

2-(5-Chloromethyl-thiophen-2-yl)-4,4,5,5-tetramethyl-[1,3]dioxolane (**11**): Thionyl chloride (7 mL, 36 mmol) was added to 0.5 g of **10** (2 mmol) and the mixture was refluxed under nitrogen for 3 h. Exsess thionyl chloride was removed under reduced pressure and the crude was re-dissolved in methylene chloride and washed with a slightly basic aqueous solution. The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The product, a yellow oil, was obtained in 53% yield (0.2 g). ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 6.97 (d, 1H), 6.91 (d, 1H), 6.10 (s, 1H), 4.75 (s, 2H), 1.28 (s, 6H), 1.26 (s, 6H).

Triphenyl-[5-(4,4,5,5-tetramethyl-[1,3]dioxolan-2-yl)-thiophen-2-ylmethyl]-phosphane (**12**): Triphenyl phosphine (0.4 g, 1.6 mmol) was added to a stirred solution of **11** (0.2 g, 0.8 mmol) in 15 mL of dry THF and the reaction was refluxed for 72 h under nitrogen. The yellow precipitate was isolated by filtration, washed with hexane and dried, affording 0.19 g of **12** (47% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.78 (m, 9H), 7.63 (m, 6H), 7.09 (d, 2H), 6.86 (d, 2H), 5.97 (s, 1H), 5.83 (s, 1H), 5.78 (s, 1H), 1.20 (s, 6H), 1.13 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 134.9, 130.2, 118.2, 117.5, 96.2, 83.0, 67.9, 25.5, 24.0, 21.9. mp > 200 °C. MS (TOF LD^+): *m/z*: 487.3 (M^+).

2,3-Dihdro-thieno[3,4-b][1,4]dioxine-5-carbaldehyde (**13**):[28] 3,4-Ethylenedioxythiophene (2 mL, 18 mmol) was dissolved in dry DMF (10 mL, 126 mmol), the solution was cooled to –10 °C and $POCl_3$ (1.76 mL, 18 mmol) was added dropwise over 15 min. The mixture was then allowed to reach room temperature then stirred for an additional hour. The reaction was poured into an ice bath and neutralized using a basic aqueous solution. The product, in the form of white needles, was filtered and dried, yielding a quantitative yield (3.06 g). ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.84 (s, 1H), 6.73 (s, 1H), 4.31 (d, 2H), 4.21 (d, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 180.0, 141.7, 110.8, 110.7, 65.2, 64.3. mp = 140 °C. MS (TOF LD+) *m/z*: 170 ($M+H^+$).

5-(5,5-Dimethyl-[1,3]dioxin-2-yl)-2,3-dihydro-thieno[3,4-b][1,4]dioxine (**14**): 2,2-dimethyl-1,3-propandiol (1.2 g, 11 mmol) and a catalytic amount of *p*-toluenesulfonic acid were added to a solution of **13** in 50 mL of toluene. The mixture was refluxed for 1 h then cooled and washed with brine. The organic phase was dried over Na_2SO_4 and evaporated. The crude was purified over alumina (7:3, hexane:methylene chloride), yielding a white solid (2.5 g, 90% yield). ^{1}H NMR (300 MHz, dimethyl sulfoxide (DMSO)-d_6, δ_{ppm}): 6.55 (s, 1H), 5.60 (s, 1H), 4.17 (m, 4H), 3.57 (s, 4H), 1.12 (s, 3H), 0.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 101.4, 97.3, 79.5, 66.6, 66.4, 24.7, 23.6. mp = 134 °C. MS: (TOF LD+) *m/z*: 256.46 ($M+H^+$).

5-Bromo-7-(5,5-dimethyl-[1,3]dioxin-2-yl)-2,3-dihydro-thieno[3,4-b][1,4]dioxine (**15**):[28] **14** (1.5 g, 5.8 mmol) was suspended in 40 mL of dry acetonitrile, at –78 °C, in the dark and under nitrogen, then NBS (1.17 g, 6.6 mmol) was added and the mixture was allowed to reach room temperature. After 20 min at room temperature, water was added and the product, a white solid, precipitated and filtered, yielding **15** in a quantitative yield (1.94 g). ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 5.58 (s, 1H), 4.17 (m, 4H), 3.67 (d, 2H), 3.52 (d, 2H), 1.18 (s, 3H), 0.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 96.9, 89.8, 79.4, 66.8, 66.5, 31.9, 24.6, 23.6. mp = 114 °C. MS (TOF LD+): *m/z*: 335.45 (M^+).

{4-[7-(5,5-Dimethyl-[1,3]dioxan-2-yl)-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl]-benzyl}-phosphonic acid diethyl ester (**16**): **15** (0.6 g, 1.8 mmol), (4-boronic acid – benzyl)-phosphonic acid diethyl ester[16] (0.49 g, 1.8 mmol), 15 mL of 2M aqueous sodium bicarbonate and $[P(Ph)_3]_2PdCl_2$ (57 mg, 0.08 mmol) were added to 30 mL of toluene. The reaction mixture was stirred at 100 °C overnight, then the organic phase was separated, dried over Na_2SO_4 and evaporated. The crude was purified over alumina (methylene chloride) affording 0.35 g of a yellow solid (45% yield). ^{1}H NMR (300 MHz, DMSO-d_6, δ_{ppm}): 7.58 (d, 2H), 7.26 (d, 2H), 5.56 (s, 1H), 4.27 (m, 4H), 3.91 (m, 4H), 3.58 (s, 4H), 3.24 (s, 1H), 3.17 (s, 1H), 1.29 (s, 3H), 1.09 (t, 6H), 0.71 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6, δ_{ppm}): 139.7, 137.8, 125.8, 115.4, 112.3, 94.7, 76.8, 65.2, 64.7, 61.8, 32.9, 31.8, 30.1, 23.0, 21.6, 16.6. mp = 113 °C. MS (TOF LD+): *m/z*: 482.31 (M^+).

7-Bromo-9,9-dioctyl-9H-fluorene-2-carbaldehyde (**17**):[29] 2.3 mL of a n-butyllithium solution (1.6 M in hexane) were added dropwise to a solution of 2,7-dibromo-9,9 dioctyl-9H-fluorene (2 g, 3.6 mmol) in 30 mL of dry THF at –78 °C under nitrogen. After stirring for 1 h at –78 °C, 0.36 mL (4.7 mmol) of dry DMF were added to the solution and it was allowed to reach room temperature overnight. The solvent was evaporated and the residue washed with several portions of methylene chloride. The combined organic layers were dried over Na_2SO_4 and evaporated. The product was purified over alumina (7:3, hexane:methylene chloride) affording 0.7 g (33% yield) of **17** in the form of a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.99 (s, 1H), 7.78 (m, 3H), 7.55 (d, 1H), 7.45 (m, 2H), 1.93 (m, 4H), 1.93 (t, 4H), 1.21 (m, 20H), 0.80 (t, 6H), 0.72 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 192.2, 154.5, 151.1, 146.3, 138.5, 135.5, 130.5, 130.4, 126.4, 123.0, 122.2, 120.0, 55.5, 40.0, 31.7, 31.5, 29.8, 29.1, 23.6, 22.6, 22.5, 14.0. MS (TOF LD+): *m/z*: 497.36 (M^+).

2-(7-Bromo-9,9-dioctyl-9H-fluorene-2-yl)-5,5-dimethyl-[1,3]dioxane (**18**): 2,2-dimethyl-1,3-propandiol (0.34 g, 3.2 mmol) and a catalytic amount of *p*-toluenesulfonic acid were added to a solution of **17** (0.8 g, 1.6 mmol) in 80 mL of toluene. The mixture was refluxed for 48 h then cooled, washed with brine, dried over Na_2SO_4 and evaporated. The product was purified over alumina (hexane). **18** (0.9 g) was isolated as a white solid in a quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.58 (d, 1H),

7.46 (m, 2H), 7.34 (m, 3H), 5.38 (s, 1H), 3.72 (d, 2H), 3.60 (d, 2H), 1.87 (t, 4H), 1.27 (s, 3H), 1.02 (m, 26H), 0.81 (m, 4H), 0.73 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 153.3, 150.2, 140.6, 139.7, 137.8, 129.8, 126.1, 125.1, 121.2, 121.1, 120.7, 102.1, 77.7, 55.4, 40.1, 31.7, 30.2, 29.8, 29.1, 29.0, 23.5, 23.0, 22.5, 14.0. mp = 62 °C. High-resolution (HR) MS (TOF ES+): *m/z*: 583.3144 (M^+).

{4-[7-(5,5-Dimethyl-[1,3]dioxan-2-yl)-9,9-dioctyl-9H-fluoren-2-yl]-benzyl}-phosphonic acid diethyl ester (**19**): **18** (1 g, 1.7 mmol), (4-boronic acid – benzyl)-phosphonic acid diethyl ester[16] (0.5 g, 1.7 mmol), 15 mL of 2 M aqueous sodium bicarbonate and $[P(Ph)_3]_2PdCl_2$ (0.4 mg, 0.00057 mmol) were added to 15 mL of toluene and the reaction mixture was kept overnight at 100 °C. The organic phase was separated, dried over Na_2SO_4 and evaporated. The product was purified over alumina (methylene chloride) yielding 1 g (80% yield) of **19** in the form of a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.72 (m, 2H), 7.62 (d, 2H), 7.53 (m, 3H), 7.45 (s, 1H), 7.40 (d, 2H), 5.47 (s, 1H), 4.06 (m, 4H), 3.83 (d, 2H), 3.68 (d, 2H), 3.24 (s, 1H), 3.19 (s, 1H), 1.99 (t, 4H), 1.35 (s, 3H), 1.26 (m, 20H), 0.89 (m, 10H), 0.83 (d, 4H), 0.81 (s, 3H), 0.79 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 153.6, 152.8, 143.1, 142.1, 142.0, 141.9, 141.4, 139.2, 1323, 132.2, 132.0, 131.9, 129.1, 127.6, 126.8, 123.2, 122.6, 121.9, 121.4, 104.1, 79.6, 64.0, 57.0, 55.2, 42.1, 35.8, 34.7, 33.6, 33.4, 32.0, 31.8, 31.0, 30.9, 25.5, 24.9, 24.4, 24.3, 23.7, 18.2, 18.1, 15.9, 15.8. HRMS (TOF ES+): *m/z*: 731.4817 (M^+H^+).

General Wittig Reaction Procedure 1: 1.8 mmol of the phosphonium salt were added to a solution of sodium ethoxide (82 mg, 3.6 mmol) in ethanol then 2 mmol of the aldehyde were added. The reaction was stirred for 1 h under nitrogen at room temperature. The solution was then evaporated and the residue extracted with methylene chloride. The organic layer was dried over Na_2SO_4 and evaporated. The product was purified using chromatography.

Trans-4,4,5,5-tetramethyl-2-(4-styryl-phenyl)-[1,3]dioxolane (**E-20**): ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.51 (m, 6H), 7.36 (t, 2H), 7.26 (d, 1H), 7.12 (s, 2H), 5.99 (s, 1H), 1.34 (s, 6H), 1.29 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 139.1, 137.7, 137.3, 128.9, 128.7, 128.4, 127.6, 126.6, 126.5, 126.4, 82.7, 99.7, 24.3, 22.2. mp = 87 °C. MS (TOF LD+): *m/z*: 308.2 (M^+).

Trans-4,4,5,5-tetramethyl-2-[4-(2-thiophen-2-yl-vinyl)-phenyl]-[1,3] dioxolanle (**E-21**): ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.44 (s, 4H), 7.18 (d, 1H), 7.05 (d, 1H), 6.98 (t, 1H), 6.92 (s,1H), 6.87 (s, 1H), 5.95 (s, 1H), 1.31 (s, 6H), 1.26 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 139.0, 128.0, 127.6, 126.6, 126.2, 124.4, 122.0, 99.7, 82.7, 24.3, 22.2. mp = 94 °C. MS (TOF LD+): *m/z*: 314.3 (M^+).

Trans-4,4,5,5-tetramethyl-2-(5-styryl-thiophen-2-yl)-[1,3]dioxolane (**E-22**): ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.46 (d, 2H), 7.36 (t, 3H), 7.26 (s, 1H), 7.16 (d, 1H), 7.03 (d,1H), 6.90 (d, 1H), 6.15 (s, 1H), 1.46 (s 6H), 1.35 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 143.6, 142.3, 136.9, 128.7, 128.5, 127.6, 126.7, 126.3, 125.7, 121.9, 96.7, 83.1, 24.3, 22.2. mp = 93 °C. MS (TOF LD$^+$): *m/z*: 314.1 (M^+).

4,4,5,5-tetramethyl-2-{4-[2-(4-styryl-phenyl)-vinyl]-phenyl}-[1,3]dioxolane (**E,E-31**): ^{1}H NMR (500 MHz, $CDCl_3$, δ_{ppm}): 7.49 (m, 10H), 7.34 (t, 3H), 7.10 (s, 4H), 5.97 (s, 1H), 1.31 (s, 6H), 1.26 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, δ_{ppm}): 139.0, 137.2, 129.4, 129.0, 128.8, 128.3, 99.8, 82.5, 21.9. mp = 98 °C. MS (TOF LD$^+$): *m/z*: 410.2 (M^+).

4,4,5,5-tetramethyl-2-(4-{2-[4-(2-thiophen-2-yl-vinyl)-phenyl]-vinyl}-phenyl)-[1,3]dioxolane (**E,E-32**): ^{1}H NMR (500 MHz, $CDCl_3$, δ_{ppm}): 7.47 (m, 8H), 7.20 (d, 1H), 7.17 (d, 1H), 7.06 (s, 2H), 7.03 (d, 1H), 6.98 (m, 1H), 6.87 (d, 1H),5.97 (s, 1H), 1.31 (s, 6H), 1.26 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, δ_{ppm}): 142.9, 129.2, 128.7, 126.6, 126.0, 124.3, 121.6, 99.8, 82.6, 24.8, 22.1. MS (TOF LD$^+$): *m/z*: 416.20 (M^+).

4,4,5,5-tetramethyl-2-{5-[2-(5-styryl-thiophen-2-yl)-vinyl]-thiophen-2-yl}-[1,3]dioxolane (**E,E-33**): ^{1}H NMR (500 MHz, $CDCl_3$, δ_{ppm}): 7.37 (d, 2H), 7.27 (t, 2H), 7.18 (s, 1H), 7.16 (s, 1H), 7.05 (d, 1H), 7.00 (s, 1H), 6.94 (m, 5H), 6.17 (s, 1H), 1.37 (s, 6H), 1.33 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, δ_{ppm}): 143.1, 141.8, 136.8, 128.5, 127.1, 127.0, 126.9, 125.7, 121.7, 121.6, 96.4, 83.0, 24.2, 22.0. MS (TOF LD$^+$): *m/z*: 422.

General Deprotection Procedure: Protected materials, such as **20–23**, were deprotected by heating their solution in a 1:2 mixture of 10% HCl:THF to 60 °C under an inert atmosphere for 3 h. The solution was neutralized using a basic aqueous solution, then evaporated. The residue was re-dissolved in methylene chloride, dried over Na_2SO_4 and evaporated. The products are normally received in a quantitative yield.

3-(2-{4-[7-(5,5-Dimethyl-[1,3]dioxin-2-yl)-2,3-dihydro-thieno[3,4-b][1,4] dioxin-5-trans-4-styryl-benzaldehyde (**E-28**): ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.93 (s, 1H), 7.82 (d, 2H), 7.61 (d, 2H), 7.50 (d, 2H), 7.35 (t, 2H), 7.30 (d, 2H), 7.05 (d, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 191.6, 143.4, 136.5, 135.6, 132.1, 130.2, 129.4, 128.7, 126.8. MS (chemical ionization (CI)): *m/z*: 208.0 (M^+).

Trans-4-(2-thiophen-2-yl-vinyl)-benzaldehyde (**E-29**): ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.98 (s, 1H), 7.80 (d, 2H), 7.52 (d, 2H), 7.35 (d,1H), 7.22 (s, 1H), 7.09 (d, 1H), 6.98 (m, 1H), 6.86 (d, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 143.1, 142.1, 135.2, 130.3, 127.8, 127.6, 126.7, 126.6, 125.7, 125.1, 2.8. MS (TOF by affinity purification (AP+)): *m/z*: 215.1 ($M+H^+$).

General Wittig Reaction Procedure 2: 2 mmol of the phosphonium salt were added to a solution of t-BuOK (0.7 g, 6 mmol) in dry THF (10 mL) and cooled to 0 °C. Then 2 mmol of the aldehyde were added. The reaction was stirred for 1 h under nitrogen at room temperature. The solution was then evaporated and the residue extracted with methylene chloride. The organic layer was dried over Na_2SO_4 and evaporated. The product was purified using chromatography.

3-(2-{4-[7-(5,5-Dimethyl-[1,3]dioxin-2-yl)-2,3-dihydro-thieno[3,4-b][1,4] dioxin-5-yl]-phenyl}-vinyl)-9-hexyl-9H-carbazole (**E-24**): ^{1}H NMR (500 MHz, DMSO-d_6, δ_{ppm}): 8.39 (s, 1H), 8.18 (d, 1H), 7.65 (m, 7H), 7.40 (d, 2H), 7.23 (s, 1H), 7.21 (m, 1H), 5.67 (s, 1H), 4.39 (m, 4H), 4.29 (t, 2H), 3.61 (s, 4H), 1.76 (m, 2H), 1.22 (m, 6H), 1.16 (s, 3H), 0.82 (t, 3H), 0.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ_{ppm}): 140.8, 140.2, 139.3, 137.3, 136.3, 131.6, 129.4, 128.5, 126.3, 125.7, 125.5, 124.4, 123.1, 122.8, 120.4, 118.9, 118.6, 117.4, 119.3, 108.8, 95.4, 77.7, 71.8, 64.7, 43.1, 31.5, 30.1, 29.6, 28.9, 26.9, 22.6, 14.1. mp = 103 °C. MS (TOF LD+): *m/z*: 607.29 (M+).

[4-(2-{4-[7-(5,5-Dimethyl-[1,3]dioxin-2-yl)-2,3-dihydro-thieno[3,4-b] [1,4]dioxin-5-yl]-phenyl}-vinyl)-phenyl]-diphenyl-amine (**E-25**): ^{1}H NMR (500 MHz, $CDCl_3$, δ_{ppm}): 7.64 (d, 2H), 7.57 (d, 2H), 7.51 (d, 2H), 7.31 (t, 4H), 7.17 (s, 1H), 7.10 (s, 1H), 7.06 (m, 6H), 6.95 (d, 2H), 4.33 (d, 2H). 4.32 (d, 2H), 3.60 (s, 4H), 1.15 (s, 3H), 0.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ_{ppm}): 149.3, 149.1, 141.2, 139.2, 137.8, 133.7, 133.4, 131.1, 129.7, 129.1, 128.4, 128.3, 128.2, 126.3, 125.4, 124.8, 119.2, 113.8, 97.2, 79.5, 66.5, 32.0, 24.7, 23.6. mp = 200 °C. MS (TOF MS ES+): *m/z*: 602.23 ($M+H^+$).

3-(2-{4-[7-(5,5-Dimethyl-[1,3]dioxan-2-yl)-9,9-dioctyl-9H-fluorene-2-yl]-phenyl}-vinyl)-9-hexyl-9H-carbazole (**E-26**): ^{1}H NMR (500 MHz, $CDCl_3$, δ_{ppm}): 8.27 (s, 1H), 8.02 (d, 1H), 7.72 (m, 7H), 7.62 (d,1H), 7.59 (s, 1H), 7.54 (d, 1H), 7.48 (d, 1H), 7.45 (s, 1H), 7.41 (m, 2H), 7.34 (s, 1H), 7.20 (s, 2H), 5.48 (s, 1H), 4.31 (t, 2H), 3.84 (d, 2H), 3.71 (d, 2H), 2.02 (t, 4H), 1.89(m, 2H), 1.36 (s, 3H), 1.18 (m, 33H), 0.88(m, 6H), 0.80(s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ_{ppm}): 153.6, 152.8, 143.2, 142.7, 142.1, 142.0, 141.9, 141.5, 139.1, 138.7, 131.4, 130.1, 129.2, 128.4, 127.6, 127.5, 127.3, 126.8, 126.2, 125.0, 124.7, 123.1, 122.6, 122.2, 121.9, 121.5, 120.8, 120.5, 110.7, 104.2, 79.6, 57.0, 55.2, 45.0, 42.1, 33.6, 33.4, 32.1, 31.85, 31.05, 31.0, 30.8, 28.7, 25.5, 24.9, 24.4, 24.3, 23.7, 15.9, 15.8. HRMS (TOF MS ES+): *m/z*: 856.6003 (M^+H^+).

[4-(2-{4-[7-(5,5-Dimethyl-[1,3]dioxan-2-yl)-9,9-dioctyl-9H-fluoren-2-yl]-phenyl}-vinyl)-phenyl]-diphenylamine (**E-27**): ^{1}H NMR (500 MHz, $CDCl_3$, δ_{ppm}): 7.77 (dd, 2H), 7.70 (d, 2H), 7.63 (d, 4H), 7.57 (d,1H), 7.50 (s, 1H), 7.46 (d, 2H), 7.30 (t, 4H), 7.16 (d, 4H), 7.14 (s, 1H), 7.12(d, 2H), 7.07 (t, 3H), 5.15 (s, 1H), 3.85 (d, 2H), 3.74 (d, 2H), 2.04 (t, 4H), 1.39 (s, 3H), 1.12 (m, 24H), 0.86 (m, 6H), 0.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ_{ppm}): 153.7, 152.8, 149.4, 149.2, 143.2, 142.3, 142.0, 141.4, 139.2, 138.4, 133.4, 131.1, 129.9, 129.2, 128.7, 128.6, 128.4, 127.5, 126.9, 126.4, 126.3, 125.4, 124.9, 123.1, 122.7, 122.0, 121.5, 104.2, 79.6, 57.1, 42.1, 33.6, 32.1, 31.8, 31.1, 31.0, 30.1, 25.6, 25.0, 24.4, 23.8, 15.9, 2.9. mp = 180 °C. MS (TOF ES+): *m/z*: 850.55 ($M+H^+$).

7-{4-[2-(4-Diphenylamino-phenyl)-vinyl]phenyl}-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-carbaldehyde, (**E-34**): **E-25** (0.3 g, 0.5 mmol) was dissolved in 1:1 water/methylene chloride bi phasic mixture (10 mL) and cooled to 0 °C. TFA (2 mL, 25 mmol) was added and the resulting mixture was stirred at rt under nitrogen for 2 h. The

methylene chloride layer was then dried over Na_2SO_4 and evaporated. The product was purified over alumina (3:7, methylene chloride:hexane) affording 0.23 g (92% yield) of **E-34** in the form of an orange solid. ^{1}H NMR (500 MHz, DMSO-d_6,δ_{ppm}): 9.87 (s, 1H), 7.80 (d, 2H), 7.66 (d, 2H), 7.54 (d,2H), 7.30 (t, 4H), 7.25 (s, 1H), 7.16 (s, 1H), 7.07 (m, 6H), 6.90 (d, 2H), 4.47(d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ_{ppm}): 181.4, 149.5, 149.2, 140.0, 139.6, 132.8, 132.2, 131.1, 131.0, 129.3, 129.0, 128.4, 127.8, 126.4, 125.1, 125.0, 117.3, 66.9, 66.4. mp = 198 °C. MS (TOF ES+): *m/z*: 516.66 ($M+H^+$).

[4-(2-{4-[7-(2-{4-[7-(5,5-Dimethyl-[1,3]dioxan-2-yl)-9,9-dioctyl-9H-fluorene-2-yl]-phenyl}-vinyl)-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl]-phenyl}-vinyl)-phenyl]-dipheyl-amine (**E,E-35**): **19** (0.32 g, 0.4 mmol) was dissolved in dry THF (10 mL), the solution was cooled to 0 °C then t-BuOK (0.15 g, 1.2 mmol) was added. After 3 min **34** (0.23 g, 0.4 mmol) in 8 mL of dry THF was added to the solution. The resulting mixture was stirred at 0 °C under nitrogen for 1 h. The solvent was removed under reduced pressure and the product was purified on alumina (3 : 7 methylene chloride : hexane) affording 0.34 g (70% yield) **E,E-35** in the form of a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ_{ppm}): 7.74 (m, 4H), 7.63 (d, 2H), 7.55 (m, 8H), 7.48 (d, 2H), 7.39 (d, 2H), 7.28 (s, 2H), 7.05 (m, 10H), 6.90 (d, 2H), 5.47 (s, 1H), 4.37 (s, 4H), 3.83 (d, 2H), 3.71 (d, 2H), 2.01 (t, 4H), 1.62 (m, 24H), 1.35 (s, 3H), 0.83 (s, 3H), 0.81 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, δ_{ppm}): 149.3, 149.1, 133.3, 131.1, 129.6, 129.1, 128.3, 127.9, 126.3, 125.4, 124.8, 99.4, 79.6, 66.6, 66.3, 33.6, 31.8, 31.0, 30.9, 24.4, 23.7, 15.9, 15.8. mp = 89 °C. MS (TOF ES+): *m/z*: 1093.41 ($M+H^+$).

7-{4-[2-(7-{4-[2-(4-Diphenylamino-phenyl)-vinyl]-phenyl}2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-vinyl]-phenyl}-9,9-dioctyl-9H-fluorene-2-carbaldehyde (**E,E-36**): **E,E-35** (0.05 g, 0.04 mmol) was dissolved in 2:1 THF: 5% HCl and heated to 70 °C for 4 h. The reaction was neutralized using an aqueous solution of $NaHCO_3$ and extracted with ether. The organic phase was dried over Na_2SO_4 and evaporated. The product was purified over silica (3:7, methylene chloride:hexane) affording 0.04 g (87% yield) of **E,E-36** in the form of a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ_{ppm}): 10.00 (s, 1H), 7.82 (m, 4H), 7.67 (d, 2H), 7.58 (m, 8H), 7.44 (d, 2H), 7.32 (d, 2H), 7.23 (s, 2H), 6.97 (m, 10H), 6.83 (d, 2H), 4.31(s, 4H), 2.01 (t, 4H), 1.20 (m, 24H), 0.73 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, δ_{ppm}): 192.2, 152.9, 151.7, 147.5, 147.3, 147.2, 141.3, 139.7, 138.7, 136.8, 135.9, 135.2, 131.8, 131.5, 129.2, 127.3, 126.5, 126.1, 124.4, 123.5, 123.0, 121.2, 115.8, 115.2, 64.8, 55.3, 40.1, 31.8, 31.6, 30.2, 30.0, 29.8, 29.7, 29.6, 29.4, 29.3, 23.7, 23.6, 14.0, 13.9. mp = 85 °C. MS (TOF ES+): *m/z*: 1006.52 ($M+H^+$).

Oligomer (**E,E,E,E-38**): Bi-functional reagent **37**[30] (0.12 g, 0.19 mmol) was dissolved in dry THF (8 mL) then the solution was cooled to 0 °C and t-BuOK (0.17 g, 1.55 mmol) was added. After 3 min **E-34** (0.2 g, 0.39 mmol) was added and the resulting mixture was stirred at rt under nitrogen for 2 h. The solvent was then removed under reduced pressure and the product was purified over alumina (3:7, methylene chloride:hexane) affording 0.13 g (53% yield) of **E,E,E,E-38** in the form of a red solid. ^{1}H NMR (500 MHz, $CDCl_3$,δ_{ppm}): 7.66 (d, 4H), 7.43 (d, 4H), 7.34 (d, 4H), 7.23 (m,12H), 7.06 (d, 8H), 6.94 (m, 14H), 4.29 (s, 8H), 3.88 (d, 4H), 1.78 (t, 2H), 1.34 (m, 4H), 1.19 (m, 12H), 0.9 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, δ_{ppm}): 151.0, 147.5, 147.2, 131.5, 129.2, 127.2, 126.4, 126.0, 124.4, 123.3, 122.9, 116.6, 71.7, 66.4, 39.8, 30.8, 29.2, 24.2, 23.1, 14.1, 11.4. mp = 262 °C. MS (TOF LD-): *m/z*: 1356.52 (M+).

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[1] V. I. Adamovich, S. R. Cordero, P. I. Djurovich, A. Tamayo, M. E. Thompson, B. W. D'Andrade, S. R. Forrest, *Org. Electron.* **2003**, *4*, 77.
[2] A. Speicher, T. Backes, S. Grosse, *Tetrahedron* **2005**, *61*, 11692.
[3] a) M. Bodanszky, A. Bodanszky, *The Practice of Peptide Synthesis*, 2nd ed., Springer, Berlin **1994**; b) L. B. Townsend, R. S. Tipson, *Nucleic Acid Chemistry: Improved and New Synthetic Procedures, Methods, and Techniques*, John Wiley and Sons, New York **1986**.
[4] T. Maddux, W. Li, L. Yu, *J. Am. Chem. Soc.* **1997**, *119*, 844.
[5] J. M. Tour, *J. Org. Chem.* **2005**, *70*, 3396.
[6] M. J. G. Escalonilla, F. Langa, J. M. Rueff, L. Oswaldb, J. F. Nierengartenb, *Tetrahedron Lett.* **2002**, *43*, 7507.
[7] M. Jorgensen, F. C. Krebs, *J. Org. Chem.* **2004**, *69*, 6688.
[8] H. Noguchi, K. Hojo, M. Suginome, *J. Am. Chem. Soc.* **2007**, *129*, 758.
[9] a) O. Deeg, P. Kirsch, D. Pauluth, P. Bauerle, *Chem. Commun.* **2002**, 2762; b) O. Deeg, P. Bauerle, *Org. Biomol. Chem.* **2003**, *1*, 1609.
[10] a) C. A. Briehn, P. Baeuerle, *Chem. Commun.* **2001**, *40*, 4680; b) C. A. Briehn, P. Baeuerle, *J. Comb. Chem.* **2002**, *4*, 457.
[11] S. Anderson, *Chem. Eur. J.* **2001**, *7*, 4706.
[12] a) J. K. Young, J. C. Nelson, J. S. Moore, *J. Am. Chem. Soc.* **1994**, *116*, 10841; b) J. C. Nelson, J. K. Young, J. S. Moore, *J. Org. Chem.* **1996**, *61*, 8160.
[13] a) N. Tessler, O. Globerman, N. Rappaport, Y. Preezant, Y. Roichman, O. Solomesch, J. Veres, S. Tal, E. Gershman, M. Adler, V. Zolotarev, V. Gorelik, Y. Eichen, in *Conjugated Polymers: Processing and Applications* (*Handbook of Conducting Polymers, 3rd Edition*) (Eds: T. A. Skotheim, J. Reynolds), CRC Press, Boca Raton, Florida **2006**, Ch. 7; b) O. Solomeshch, Y. J. Yu, V. Medvedev, A. Razin, B. Blumer-Ganon, Y. Eichen, J. I. Jin, N. Tessler, *Synth. Met.* **2007**, *157*, 841.
[14] G. Lai, X. R. Bu, J. Santos, E. A. Mintz, *Synlett* **1997**, *11*, 1275.
[15] a) H. Meier, H. C. Holst, A. Oehlhof, *Eur. J. Org. Chem.* **2003**, 4173; b) L. Wen, M. Li, J. B. Schlenoff, *J. Am. Chem. Soc.* **1997**, *119*, 7726.
[16] F. C. Krebs, M. Jorgensen, *Macromolecules* **2002**, *35*, 10233.
[17] R. Koike, Y. Katayose, A. Ohta, J. Motoyoshiya, Y. Nishii, H. Aoyama, *Tetrahedron* **2005**, *61*, 11020.
[18] A. J. Bard, L. R. Faulkner, in *Electrochemical Methods: Fundamentals and Applications*, Wiley, New-York **2000**.
[19] J. Roncali, *Chem. Rev.* **1997**, *97*, 173.
[20] H. Sirringhaus, N. Tessler, R. H. Friend, *Science* **1998**, *280*, 1741.
[21] N. Tessler, V. Medvedev, M. Kazes, S. Kan, U. Banin, *Science* **2002**, *295*, 1506.
[22] C. R. Newman, C. D. Frisbie, D. A. da silva Filho, J. L. Brdas, P. C. Ewbank, K. R. Mann, *Chem. Mater.* **2004**, *16*, 4436.
[23] T. Mori, *J. Phys.: Cond. Mat.* **2008**, *20*, 184010.
[24] a) Y. Roichman, N. Tessler, *Appl. Phys. Lett.* **2002**, *80*, 151; b) A. L. Holt, J. H. Leger, S. A. Carter, *J. Chem. Phys.* **2005**, *123*, 044704.
[25] S. Shaked, S. Tal, Y. Roichman, A. Razin, S. Xiao, Y. Eichen, N. Tessler, *Adv. Mater.* **2003**, *15*, 913.
[26] a) X. M. Hong, H. E. Katz, A. J. Lovinger, B.C. Wang, K. Raghavachari, *Chem. Mater.* **2001**, *13*, 4686; b) M. Mushrrush, A. Facchetti, M. Lefenfeld, E. H. Katz, T. J. Marks, *J. Am. Chem. Soc.* **2003**, *125*, 9414; c) M. Ichikawa, H. Yanagi, Y. Shimizu, S. Hotta, N. Suganuma, T. Koyama, Y. Taniguchi, *Adv. Mater.* **2002**, *14*, 1272.
[27] G. P. Bartholomew, M. Rumi, S. J. K. Pond, J. W. Perry, S. Tretiak, G. C. Bazan, *J. Am. Chem. Soc.* **2004**, *126*, 11529.
[28] M. Jessing, M. Brandt, K. J. Jensen, J.B. Christensen, U. Boas, *J. Org. Chem.* **2006**, *71*, 6734.
[29] C. Van Der Pol, M. R. Bryce, M. Wielopolski, C. A. Castellonos, D. M. Guldi, S. Filippone, N. Martin, *J. Org. Chem.* **2007**, *72*, 6662.
[30] R. Koike, Y. Katayose, A. Ohta, J. Motoyoshiya, Y. Nishii, H. Aoyama, *Tetrahedron* **2005**, *61*, 11020.
[31] J. C. deMello, H. F. Wittmann, R. H. Friend, *Adv. Mater.* **1997**, *9*, 230.
[32] R. C. Jaeger, *Introduction to Microelectronic Fabrication*, Prentice Hall, New Jersey **2002**.