Sequence-Independent Synthesis of π-conjugated Arylenevinylene Oligomers using Bifunctional Thiophene Monomers

*Kammasandra Nanjunda Shivananda, Irit Cohen, Elena Borzin, Yulia Gerchikov, Michal Firstenberg, Olga Solomeshch, Nir Tessler, and Yoav Eichen**

Sequence-independent or "click" chemistry is applied for the preparation of a series of novel and structurally similar π-conjugated oligomers. The new oligomers are prepared using Wittig–Horner chemistry from bifunctional building blocks that can be interconnected to one another at any desired sequence. The bifunctional building blocks consist of aromatic skeletons with acetal protected aldehyde groups on one side and a phosphonic acid diethyl ester group *para* to the aldehyde functionality. The first step in the arylenevinylene formation is a Wittig–Horner coupling of a functionalized aldehyde with the methyl phosphonate ester ylide of a bifunctional monomer. A stepwise protection–deprotection process is applied for the preparation of structurally similar π-conjugated oligophenylene vinylenes. New di-, tri-, penta-, and hepta-phenylenevinylenes are prepared and characterized. Selected penta-arylenevinylenes are incorporated as the semiconductor channel in organic field-effect transistors.

1. Introduction

Over the past decade π-conjugated arylene and arylenevinylene oligomers and polymers have generated considerable attention because of their possible applications in organic electronics such as light-emitting diodes,[1] organic lasers,[2] field-effect transistors (FET),[3] sensors,[4] and photovoltaic cells.[5] Despite the considerable diversity available in the structures of these materials, most of the research is limited to very simple sequences, mostly homo-oligomers and homo-polymers. This stems mainly from the increasing complexity of synthesis and purification as one moves to more complex sequences of larger building blocks.[6] As a result, it is widely accepted that synthesis is still a major obstacle for the full realization of the potential embedded in organic optoelectronics and molecular nanoelectronics.[7] Assembly by design (i.e., engineering) of complex structures with molecular, electronic grade precision is expected to open new frontiers in organic electronics by offering new families of materials to the organic electronics world.[8]

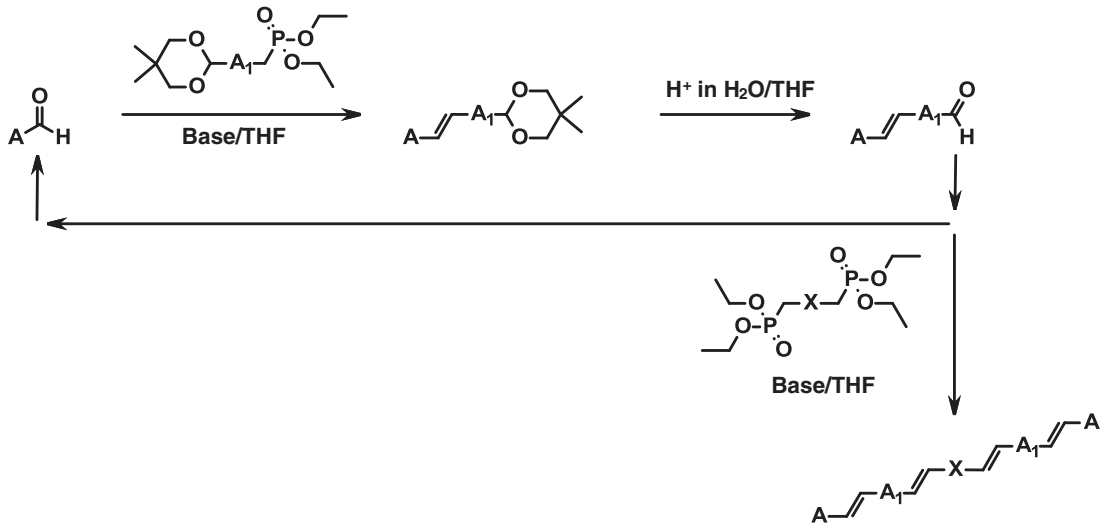
In nature, most chemical entities are prepared by target-specific machinery that is tailored to produce one material or a very narrow set of structurally similar compounds in a "copy exact" manner. This approach is being utilized in most cases where high-fidelity in synthesis is required, as can be seen in the biosynthesis of most small molecules. On the other hand, the survival of the biological realm depends on versatility, therefore nature utilizes "click"-type chemistry when dealing with producing the molecular basis of diversity, polynucleic acids and proteins.[9] In this case, nature's machinery produces highly complex materials out of a limited number of bifunctional building blocks. The biosynthesis of these materials proceeds in a way that is virtually independent of the sequence that is being prepared, much like the way LEGO bricks are assembled to one another to form various structures.[10]

Adopting such a strategy in the preparation of organic electronic materials is expected to allow us to build complex π-conjugated structures and fine tune these materials in ways that have only before been seen in nature.[11]

The application of sequence-independent chemistry to the preparation of π-conjugated electronic materials has been previously reported by several groups. Alternating Heck and Horner–Wadsworth–Emmons (HWE) reactions were applied by Yu et al. for the stepwise construction of oligo (*p*-phenylene-vinylene)s from two different bifunctional monomers.[12] Following a similar approach, Tour et al. prepared a large library of phenylene vinylene derivatives.[13] A similar stepwise Wittig–Horner protection–deprotection process was utilized by Nierengarten et al.[14] wherein the synthesis of new dumbbell-shaped di-(pyrazolino-[60] fullerene)–oligo-phenylene vinylenes was reported. Krebs et al.[15] has prepared oligo-phenylene vinylenes for solar cell applications using a similar approach; Suginome[16] used a protection-deprotection version of the Suzuki-Miyora coupling reaction to make

Dr. K. N. Shivananda, I. Cohen, Dr. E. Borzin, Y. Gerchikov, Dr. M. Firstenberg, Prof. Y. Eichen
Schulich Faculty of Chemistry
Technion- Israel Institute of Technology
Technion City, 32000 Haifa, Israel
E-mail: chryoav@tx.technion.ac.il
Dr. O. Solomeshch, Prof. N. Tessler
Nanoelectronics Center
Department of Electrical Engineering
Technion- Israel Institute of Technology Technion City
32000 Haifa, Israel

DOI: 10.1002/adfm.201101897



Scheme 1. Schematic illustration of the sequence-independent Wittig–Horner process using bifunctional monomers.

oligoarenes; and Bäuele et al.[17] used combinatorial parallel synthesis and constructed a library of 16 and 256 tetramers as candidates for a liquid crystal devices. A combinatorial synthesis on solid support was used by Bäuerle et al.[18] and Anderson et al.[19] to make a library of oligo-thiophenes and phenylene ethynylene pentamers respectively, both showing promising optoelectronic properties. Young et al. and Moore et al.[20] utilized a similar method to prepare oligomers (1,3-phenylene ethynylene) on solid support. Recently we reported on the use of solution synthesis of oligo π-conjugated peptides as well as the Wittig–Horner synthesis of oligo-phenylene vinylenes for making and optimizing new materials for electrical and electrooptical applications.[21]

The general protection-deprotection Wittig–Horner process using bifunctional monomers is outlined in **Scheme 1**. A first group **A**, bearing an aldehyde moiety, is reacted with a bifunctional π-conjugated monomer, $\mathbf{A}_1$, bearing a protected aldehyde on its one side and a diethoxy phosphoryl methyl group in the 4 position.

After the first coupling step and formation of the new double bond, the product is deprotected to release the aldehyde group of the di-arylenevinylenes for a subsequent step. This sequence may be repeated with the deprotected product of the preceding step as the starting material for subsequent reaction, using any bifunctional monomer, $\mathbf{A}_n$, to construct an oligo-phenylenevinylene of any desired sequence. Additionally, at any stage, the deprotected oligomer can be coupled with a bifunctional aromatic/nonaromatic system, **X**, bearing two diethoxy phosphoryl methyl groups, producing symmetrical oligo-phenylenevinylenes.

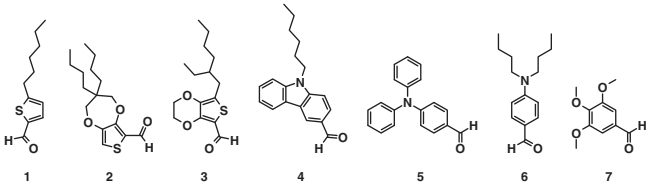
Here, we apply the Wittig–Horner sequence-independent double-bond formation to the preparation of structurally controlled functional oligomers using two new bifunctional thiophene monomers. By fabricating field-effect transistors of these oligomers, we demonstrate the potential inherent to this approach.

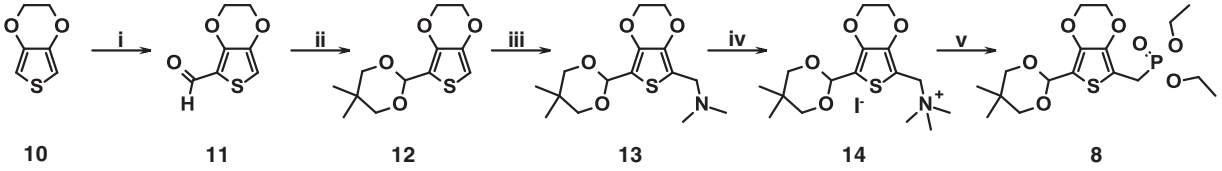
2. Results and Discussions

2.1. Materials

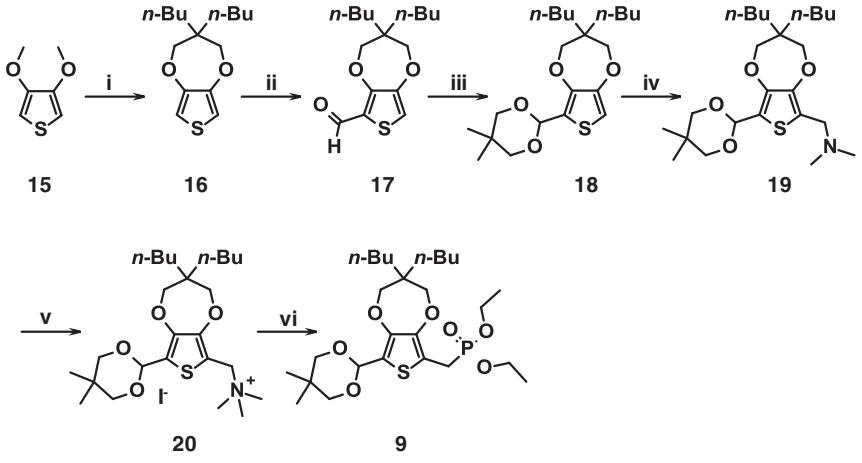
2.1.1. Mono Aldehydes

5-Hexylthiophene-2-carbaldehyde, **1**; 3,3-dibutyl-3,4-dihydro-2H-thieno [3,4-b][1,4] dioxepine-6-carbaldehyde, **2**;[22] 7-(2-ethylheptyl)-2,3-dihydrothieno [3,4-b][1,4]dioxine-5-carbaldehyde, **3**;[23] 9-hexyl -9H-carbazole -3-carbaldehyde, **4**;[24] 4-diphenylamino-benzaldehyde, **5**;[25] 4-(dibutylamino) benzaldehyde, **6**; and 3,4,5-trimethoxybenzaldehyde, **7**, were used as the starting groups for the unidirectional process.





Scheme 2. Preparation of bifunctional monomer 8: i) $POCl_3$/DMF, –10 °C to room temperature, quantitative yield; ii) 2,2-dimethyl-propane-1,3-diol, *p*-toluenesulfonic acid, refluxing toluene, quantitative yield; iii) dimethylimminium chloride, 1:1 dichloromethane:CH_3CN, 80 °C to r.t, quantitative yield; iv) CH_3I, 1:1 $CHCl_3$:Et_2O, quantitative yield; and v) $P(OCH_2CH_3)_3$, refluxing DMF, quantitative yield.



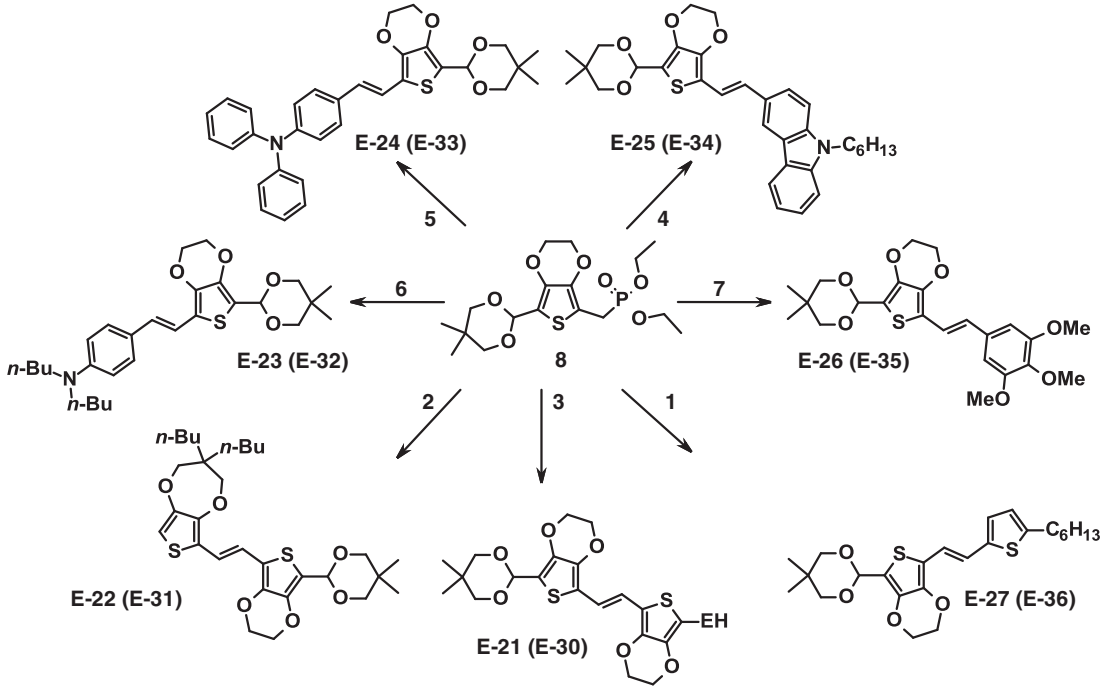
Scheme 3. Preparation of bifunctional monomer **9**: i) 2,2-dibutylpropane-1,3-diol, *p*-toluenesulfonic acid, refluxing toluene, 80% yield; ii) $POCl_3$/DMF, –10 °C to r.t, quantitative yield; iii) 2,2-dimethyl-propane-1,3-diol, *p*-toluenesulfonic acid, refluxing toluene, quantitative yield; iv) dimethylimminium chloride, CH_3CN, 80 °C to r.t, quantitative yield; v) CH_3I, 1:1 $CHCl_3$:Et_2O, quantitative yield; and vi) $P(OCH_2CH_3)_3$, refluxing DMF, quantitative yield.

2.1.2. Bifunctional Monomers

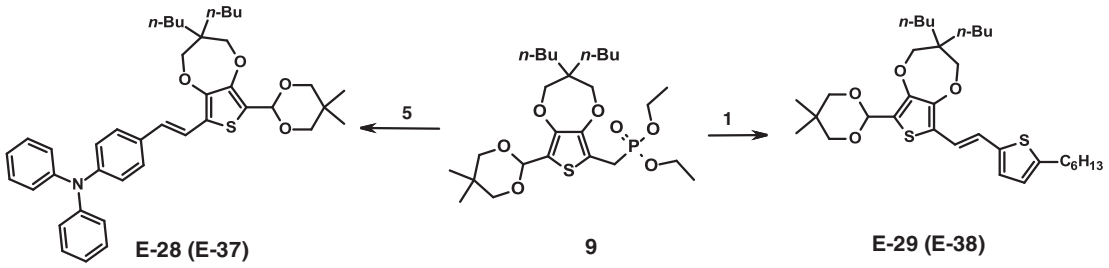
Bifunctional monomers **8** and **9** were prepared according to **Scheme 2** and **3** respectively. 3,4-ethylenedioxy thiophene (EDOT), **10**, was reacted with $POCl_3$ and dimethlyformamide (DMF) to obtain EDOT-aldehyde **11** by Vilsmeier reaction.[26] The aldehyde group of **11** was then protected with 2,2-dimethyl-1,3-propandiol under acidic conditions to afford the acetal-protected EDOT, **12**. **12** was reacted with dimethyl imminium chloride in dichloromethane to yield the *N,N*-dimethyl aminomethyl thiophene derivative **13**, which was subsequently treated with methyl iodide to yield the ammonium salt **14**. Reaction between **14** and triethyl phosphite in dry DMF afforded bifunctional monomer **8**. The same approach was applied to synthesis of bifunctional monomer **9** starting from 3,4-dimethoxythiophene, **15**, instead of 3,3-dibutyl-2,4-dihydrothieno[3,4-b][1,4] dioxepine, **16**. Both bifunctional monomers consist of a π-conjugated backbone bearing two functional groups, a diethoxy phosphoryl methyl group and an acetal protected aldehyde, rendering them suitable for recurrent Wittig–Horner reactions.

2.1.3. Di-arylenevinylenes

Nine di-arylenevinylenes were prepared by coupling bifunctional monomers **8** and **9** with aldehydes **1**–**7**. All nine coupling reactions were performed using the same conditions: *t*-BuO^-K^+, THF, 1 h at –10 °C, under inert atmosphere (**Scheme 4** and **5**). The NMR spectra of the crude mixture suggests the formation of **E-21**–**E-29** (**E** isomers) proceeds to completion without the formation of by-products. In a subsequent step, the di-arylenevinylenes were deprotected to release their aldehyde moiety and prepare them for the next Wittig–Horner reaction. All nine protected aldehydes, **E-21**–**E-29**, were deprotected using the same conditions in a mixture of tetrahydrofuran (THF, 10 mL)



Scheme 4. The synthesis of di-arylenevinylenes **E-21** to **E-27** and **E-30** to **E-36** using the bifunctional monomer 7-(diethoxy phosphoryl methyl)-5-(5,5-dimethyl-1,3-dioxan-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine, 8, and monoaldehydes **1**–**7**. In brackets: the number of the respective deprotected di-arylenevinylene aldehydes. Reaction conditions: Coupling: potassium *t*-butoxide (*t*-BuOK), THF, 1 h at –10 °C; Deprotection: THF, 1:10 HCl in H_2O.

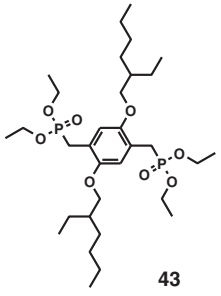


Scheme 5. The synthesis of di-arylenevinylenes **E-28** and **E-29** and **E37** and **E-38** using the bifunctional 8-(diethoxy phosphoryl methyl)-6-(5,5-dimethyl-1,3-dioxan-2-yl)-3,3-dimethyl-2,4-dihydrothieno[3,4-b][1,4] dioxepine monomer, **9**, and monoaldehydes **1** and **5**. In brackets: the number of the respective deprotected di-arylenevinylene aldehydes. Reaction conditions: Coupling: *t*-BuO$^-$K$^+$, THF, 1 h at –10 °C; Deprotection: THF, 1:10 HCl in H_2O.

and 1:10 HCl in H_2O (10 mL). The solution was stirred for 1 h at room temperature, yielding the nine aldehydes, **E-30**–**E-38**, respectively.

2.1.4. Tri-arylenevinylenes

Protected tri-arylenevinylenes **E,E-39** and **E,E-40** were prepared by coupling bifunctional monomer **8** with deprotected di-arylenevinylene aldehydes, **E-31** and **E-36**, under the same conditions that were used for the preparation of the protected di-arylenevinylene (**Scheme 6**). NMR spectra of the crude reaction mixtures shows that the reactions proceed to completion. Deprotected tri-arylenevinylenes **E,E-41** and **E,E-42** were obtained by using the conditions used for the deprotection of the di-arylenevinylenes.

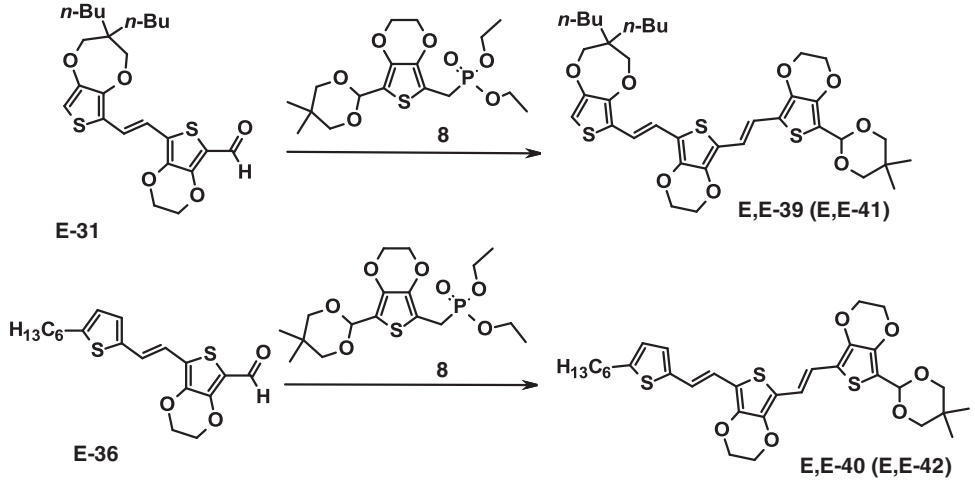


2.1.5. Penta-arylenevinylenes

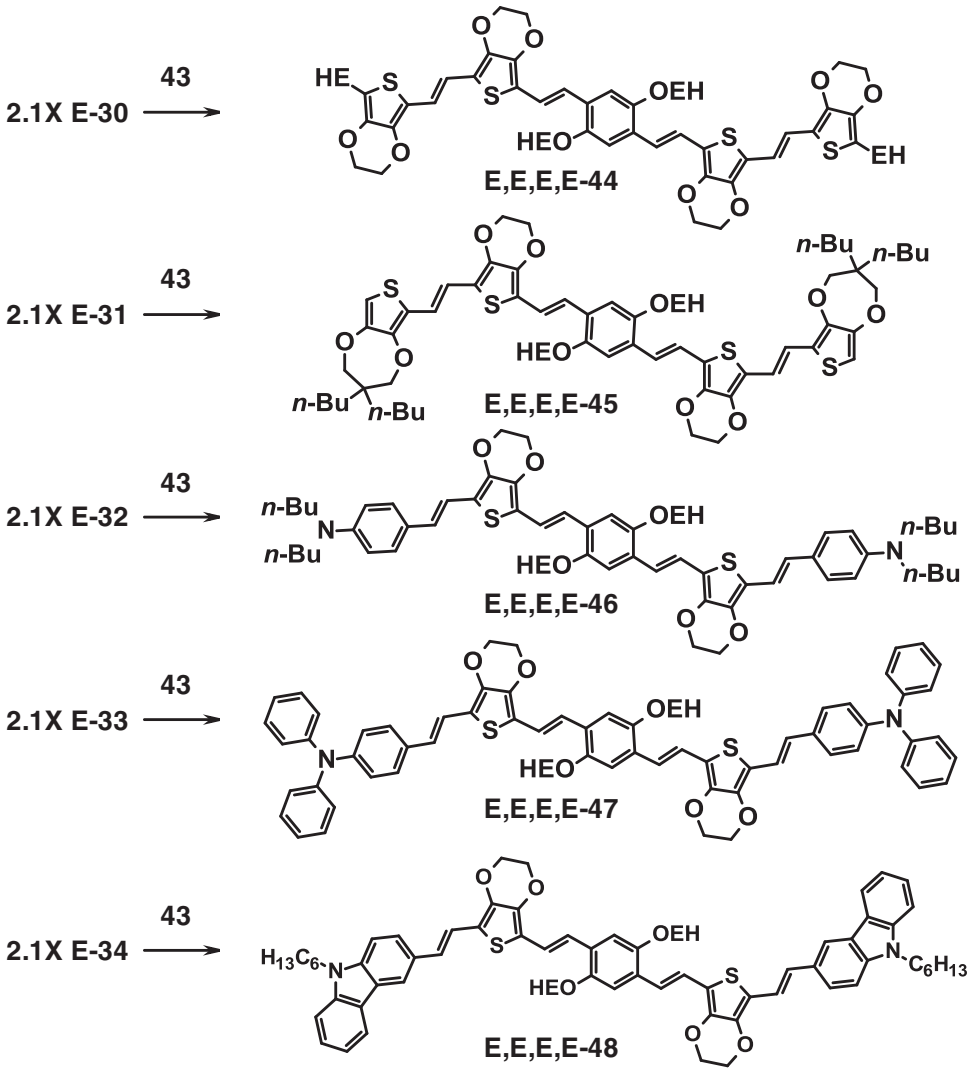
Penta-arylenevinylenes were prepared by coupling deprotected di-arylenevinylene aldehydes **E-30**–**E-38** with bifunctional diethoxy phosphoryl methyl 1,4-bis(diethoxy phosphoryl methyl)-2,5-bis(2-ethylhexoxy)benzene, **43**[27] (**Scheme 7** and **8**). All the reactions were performed by using the following conditions: **43** (1 eq.) was dissolved in dry THF under inert atmosphere at –10 °C, followed by the addition of *t*-BuO$^-$K$^+$ (4 eq.) to the solution, turning its color deep red. The respective deprotected aldehyde (2.1 eq.) was added to the solution and the mixture was stirred for 30 min at –10 °C. NMR spectra of the crude reaction mixtures of **E,E,E,E-44**–**E,E,E,E-52** shows quantitative conversion of the respective starting materials.

2.1.6. Hepta-arylenevinylenes

Hepta-arylenevinylenes were prepared by coupling deprotected tri-arylenevinylene aldehydes **E,E-41** and **E,E-42** with bifunctional diethoxy phosphoryl methyl-1,4-bis(diethoxy phosphoryl methyl)-2,5-bis(2-ethylhexoxy)benzene, **43**[27] (**Scheme 9**). The reactions were performed using the same conditions used for the preparation of the protected di- and tri-arylenevinylenes



Scheme 6. The synthesis of tri-arylenevinylenes **E,E-39** and **E,E-40** and **E,E-41** and **E,E-42** using the bifunctional 7-(diethoxy phosphoryl methyl)-5-(5,5-dimethyl-1,3-dioxan-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine monomer **8** and di-arylenevinylene aldehydes **E-31** and **E-36**. In brackets: the number of the respective deprotected tri-arylenevinylene aldehydes. Reaction conditions: Coupling: *t*-BuOK, THF, 1 hr at –10 °C; Deprotection: THF, 1:10 HCl in H_2O.



Scheme 7. The synthesis of penta-arylenevinylenes **E,E,E,E44** to **E,E,E,E-48** using the bifunctional diethoxy phosphoryl methyl 1,4-bis(diethoxy phosphoryl methyl)-2,5-bis(2-ethylhexoxy) benzene monomer, 43, and di-arylenevinylene aldehydes **E-31** to **E-34**. Reaction conditions: *t*-BuOK, THF, 30 min at –10 °C.

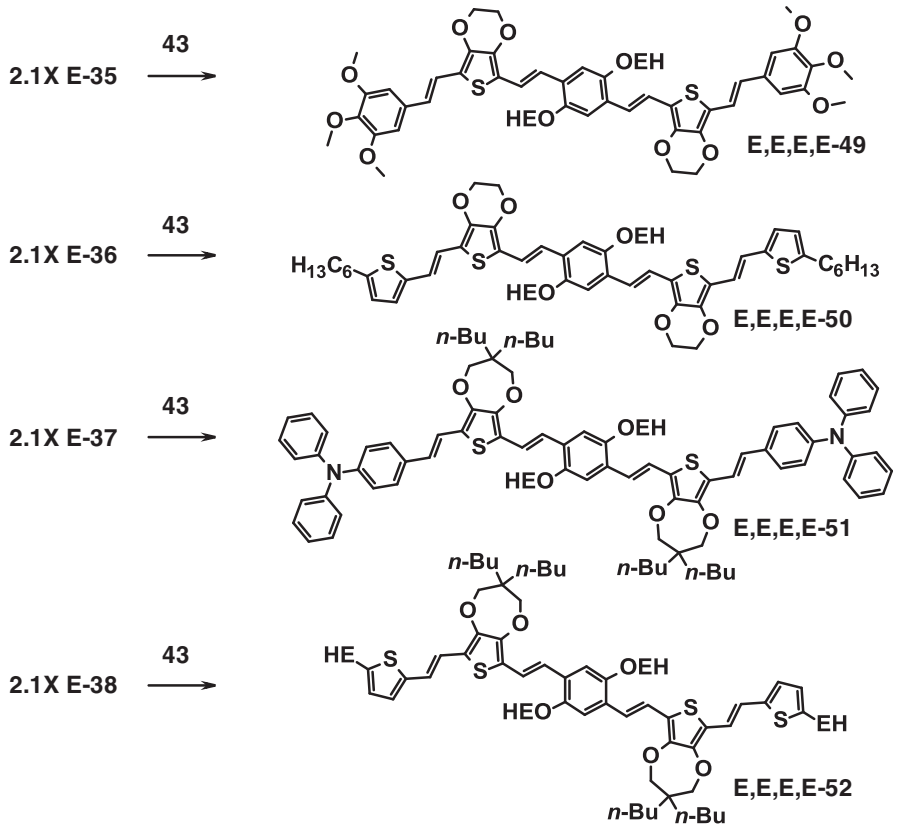
with the exception that, similar to the case of the preparation of penta-arylenevinylenes, the aldehyde was added to the reaction mixture in a 2.1:1 excess with respect to the phosphonate. Here, as well, NMR spectra of the crude reaction mixtures of **E,E,E,E,E-53**–**E,E,E,E,E,E-54** clearly show that the reactions proceeded to completion.

2.2. Optical and Electrical Characterization of the New Oligomers

The absorption and emission spectral data of protected di-arylenevinylenes **E-21**–**E-27** and deprotected di-arylenevinylenes **E-30**–**E-36**, penta-arylenevinylenes **E,E,E,E-44**–**E,E,E,E-52**, and hepta-arylenevinylenes **E,E,E,E,E-53** and **E,E,E,E,E,E-54** are shown in **Figure 1**. The electronic and optical properties of the different penta-arylenevinylenes and hepta-arylenevinylenes are presented in **Table 1**, as well as the absorption and emission maxima of **E,E,E,E-44**–**E,E,E,E-54**. The electronic levels of the different oligomers were deduced from the absorption edge in their absorption spectra, and from their cyclic voltammograms. 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 2** depicts the energy of the absorption band-edge as a function of the inverse number of double bonds in the two oligomer series **E-22**, **E-31**, **E,E,E,E-45**, **E,E,E,E,E,E-53** and **E-27**, **E-36**, **E,E,E,E-50**, **E,E,E,E,E,E-54**. Linear dependencies are observed in both cases. It is clearly seen that regardless of the increasing number of units in arylenevinylenes, the difference between two similar oligomers is negligible.

2.3. Organic Field-Effect Transistors

Organic field-effect transistors (OFETs)[28,29] were fabricated in a bottom-contact configuration[30] by spin-coating an 80 nm thick film of penta-arylenevinylenes atop an OFET structure



Scheme 8. The synthesis of penta-arylenevinylenes **E,E,E,E-49** to **E,E,E,E-52** using the bifunctional diethoxy phosphoryl methyl 1,4-bis(diethoxy phosphoryl methyl)-2,5-bis(2-ethylhexoxy) benzene monomer, **43**, and di-arylenevinylene aldehydes **E-35** to **E-38**. Reaction conditions: *t*-BuOK, THF, 30 min at –10 °C.

using a previously described procedure.[31] Penta-arylenevinylenes **E,E,E,E-44**–**E,E,E,E-52** function as the hole conducting channel in the p-type FET, which is switched on at negative gate-source voltages.

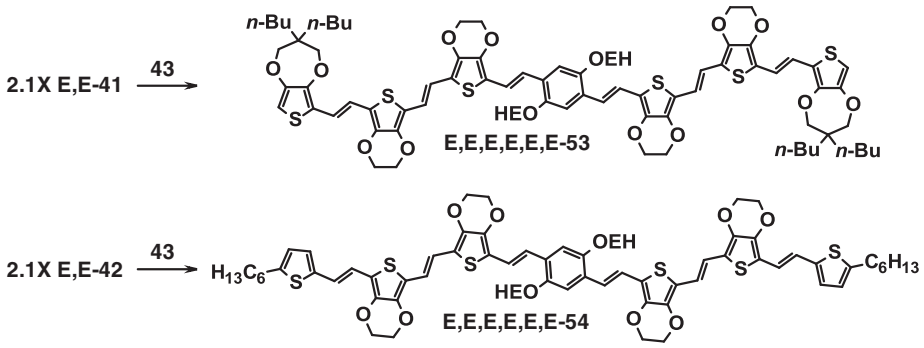
Figure 3i depicts the transfer characteristics, i.e., the drain-source currents (I_{DS}), of an OFET containing penta-arylenevinylene **E,E,E,E-50** as the semiconducting channel, as a function of gate-source voltage (V_G) for several drain-source voltages (V_{DS} = from –2 to –10 V). Figure 3ii depicts the I_{DS} in the OFET as a function of V_{DS} for different V_G values (V_G = from 0 to –20 V). By examining Figure 3i,ii, one can see that the transistor characteristics are not ideal, as there is the presence of some contact resistance (slight diode effect in Figure 3ii). Nevertheless, as a material characterization, one can still extract the charge (holes) mobility of **E,E,E,E-50** from the transfer curves, either in the linear or saturation regime:

$$\mu = \begin{cases} \dfrac{I_{DS}}{\frac{W}{L} C_{ins} \left[(V_{GS} - V_T) V_{DS} - \frac{V_{DS}^2}{2} \right]} & \text{Linear regime} \\ \dfrac{I_{DS\_SAT}}{\frac{W}{L} C_{ins} [V_g - V_T]^2} & \text{Saturation regime} \end{cases} \quad (1)$$

Where μ is the mobility, $W = 10$ mm and $L = 4$ μm are, respectively, the effective length and separation of the electrodes, and capacity of the insulation layer C_{ins} = 40 nF cm^{-2}. By extrapolating the current to zero in the linear regime, we may deduce a threshold voltage (V_T) value of approximately –5.8 V. Using this value for V_T and Equation **(1)**, the mobility in the linear regime (V_{DS} = –4 V, V_{GS} = –11 V, I_{DS} = 6.49 μA) for **E,E,E,E-50** was calculated to be about $\mu = 1 \times 10^{-3}$ cm^2 V^{-1} s^{-1}. Mobility values for **E,E,E,E-44** to **E,E,E,E-49** were calculated in the same manner and found to be 2 to 5 orders of magnitude lower, a difference we largely attribute to film morphology properties.

3. Conclusion

A stepwise, protection–deprotection, Wittig–Horner sequence independent methodology was applied for the preparation of a series of structurally similar π-conjugated di-, tri-, penta-, and hepta-arylenevinylene oligomers using two new bifunctional monomers, **8** and **9**. The synthesis procedures consist of only two different high-yield and general steps of deprotection of the aldehyde and subsequent double-bond formation. The new optical and electrochemical properties of the new oligomers were characterized, demonstrating the ability to fine-tune and optimize the optical properties as well as the HOMO and LUMO band positions. The potential embedded in using such a sequence-independent approach is also demonstrated in applying selected penta-arylenevinylenes as the semiconductor channel in OFETs. The results clearly indicate that fine-tuning the structure of the oligomer one can improve the transistor properties and hole mobility by several orders of magnitude. Efforts are currently directed towards a better understanding of the structure–hole-mobility correlation



Scheme 9. The synthesis of hepta-arylenevinylenes **E,E,E,E,E,E-53** and **E,E,E,E,E,E-54** using the bifunctional diethoxy phosphoryl methyl 1,4-bis(diethoxy phosphoryl methyl)-2,5-bis(2-ethylhexoxy) benzene monomer, **43**, and tri-arylenevinylene aldehydes **E,E-41** to **E,E-42**. Reaction conditions: *t*-BuO$^-$K$^+$, THF, 30 min at –10 °C.

with the aim of establishing a general approach to high tailoring high-mobility organic semiconductors.

4. Experimental Section

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) MS Technologies. Waters LCT Premier electrospray ionization (ESI) flow 0.2 mL min^{-1} acetonitrile:H_2O (50:50). Melting points were recorded on a DSC (differential scanning calorimetry) machine. Absorption and emission spectra were recorded on a UV-1601, UV-visible spectrometer (Shimadzu) and a Fluorolog (Jobin Yvon) luminescence spectrometer respectively. All optical measurements were performed in analytical grade solvents. Cyclic voltammograms were recorder by using a PGSTAT12 (Autolab) system. The three electrode electrochemical cell included an $Ag/AgNO_3$ (10^{-2} M in acetonitrile) reference electrode, a Pt (diameter $\Phi = 3$ mm) working electrode and a Pt counter electrode.

Solution processing and all film/devices are made in a nitrogen glove-box (LABMASTER 130, M. Braun, GmbH, Germany) integrated with a thermal evaporator. The substrates of the FET devices were prepared using photolithography. All current–voltage characteristics of FETs were recorded using a 4155B semiconductor parameter analyzer (Agilent).

Materials: All 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.

5-hexylthiophene-2-carbaldehyde, **1**,[26] 3,3-dibutyl-3,4-dihydro-2H-thieno[3,4-b][1,4]di-oxepine-6-carbaldehyde, **2**,[22] 7-(2-ethylheptyl)-2,3-dihydrothieno [3,4-b][1,4]dioxine-5-carbaldehyde, **3**,[26] 9-hexyl-9H-carbazole-3-carbaldehyde,**4**,[26] 4-diphenylamino-benzal dehyde, **5**,[26] 4-(dibutylamino)benzaldehyde, **6**, and 3,4,5-trimethoxybenzaldehyde, **7**, were used as the first monomers for the unidirectional process. 2,3-Dihydro-thieno[3,4-b][1,4]dioxine-5-carbaldehyde, **11**[26] and 3,3-dibutyl-3,4-dihydro-2H-thieno[3,4-b][1,4] dioxepine, 16,[32] were prepared according to a reported procedures.

5-(5,5-Dimethyl-[1,3]dioxin-2-yl)-2,3-dihydro-thieno[3,4-b][1,4]dioxine, **12**: A solution of 2,2-dimethyl-1,3-propandiol (1.2 g, 11 mmol), **11** (1 g, 5.8 mmol) and a catalytic amount of *p*-toluenesulfonic acid in toluene (50 mL) was refluxed for 1 h at 110 °C. The reaction mixture was then cooled to room temperature, washed with brine, and extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (alumina; 30% dichloromethane in hexane) yielding **12** in the form of a white solid (quant).

^{1}H NMR (300 MHz, $CDCl_3$, 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 (125 MHz, $CDCl_3$, δ_{ppm}): 101.4, 97.3, 79.5, 66.6, 66.4, 24.7, 23.6; MS (TOF LD+) *m/z*: 257.46 $[M+H]^+$; mp = 134 °C.

(2,3-Dihydro-5-(5,5-dimethyl-1,3-dioxan-2-yl)thieno[3,4-b][1,4] dioxin-7-yl)-N,N-dimethylmethanamine, **13**: A solution of dimethylimminium chloride (0.54 g, 5.85 mmol) in acetonitrile (10 mL) was added slowly, at room temperature and under an inert atmosphere, to a solution of **12** (1 g, 3.9 mmol) in dichloromethane (20 mL). A white precipitate formed, and then the solution was refluxed for 1 h and cooled to room temperature. Et_3N (10 mL) was added to the solution and the mixture was stirred for an additional 30 min at room temperature. The product was extracted from the reaction mixture with DCM, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was subsequently used as-is for the next step.

^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 6.51 (s, 1H), 5.61 (s, 1H), 4.17 (m, 4H), 3,72 (d, 2H), 3.64 (d, 2H), 2.25 (s, 6H), 1.12 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 101.4, 97.3, 79.5, 55.2, 66.6, 66.4, 42.3, 24.7, 23.6; MS (TOF LD+) *m/z*: 314.1 $[M+H]^+$.

[7-(5,5-Dimethyl-[1,3]dioxan-2-yl)-2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-ylmethyl]-trimethyl-iodine-amine, 14: An excess of methyl iodide was added to a solution of **13** (330 mg, 0.83 mmol) in a mixture of $CHCl_3$ (10 mL) and Et_2O (15 mL). After stirring the mixture for 12 h in the dark, the precipitate was filtered and washed with Et_2O, yielding **14** in the form of white crystals (quant).

^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 6.51 (s, 1H), 5.61 (s, 1H), 4.17 (m, 4H), 3.57 (d, 2H), 3.45 (d, 2H), 2.25 (s, 9H), 1.12 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 101.4, 97.3, 79.5, 55.2, 66.6, 66.4, 42.3, 24.7, 23.6; MS (TOF LD+) *m/z*: 456.1 $[M+H]^+$; mp > 250 °C.

Diethyl(2,3-dihydro-5-(5,5-dimethyl-1,3-dioxan-2-yl)thieno[3,4-b][1,4] dioxin-7-yl)methylphosphonate, **8**: A solution of **14** in dry DMF (15 mL) and triethyl phosphite (10 mL) was stirred overnight at 150 °C under an inert atmosphere, and then cooled to room temperature. An excess of DMF and triethyl phosphite were removed under reduced pressure and water was added to the mixture. The crude product was extracted with Et_2O and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was washed with hexane in order to remove traces of triethyl phosphite. The product was purified by column chromatography (alumina; 100% DCM) yielding **8** in the form of a yellowish oil (quant).

^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 5.58 (s, 1H), 4.13 (s, 4H), 4.03 (m, 4H), 3.64 (d, 2H), 3.51 (d, 2H), 3.15 (s, 1H), 3.08 (s, 1H), 1.23 (t, 6H), 1.19 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 138.4, 138.1, 112.1, 106.8, 95.1, 76.7, 64.6, 62.3, 29.8, 24.7, 21.2, 16.1; MS (TOF LD+) *m/z*: 407.2 $[M+H]^+$.

3,3-Dibutyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6-carbaldehyde, **17**: $POCl_3$ (1.76 mL, 18 mmol) was added dropwise to the stirred suspension of **16**, (2 mL, 18 mmol) in DMF (15 mL) at –10 °C under nitrogen atmosphere. The mixture was stirred for an additional 2 h at room temperature, then poured into ice and neutralized. The product was extracted with dichloromethane, dried over anhydrous Na_2SO_4 and

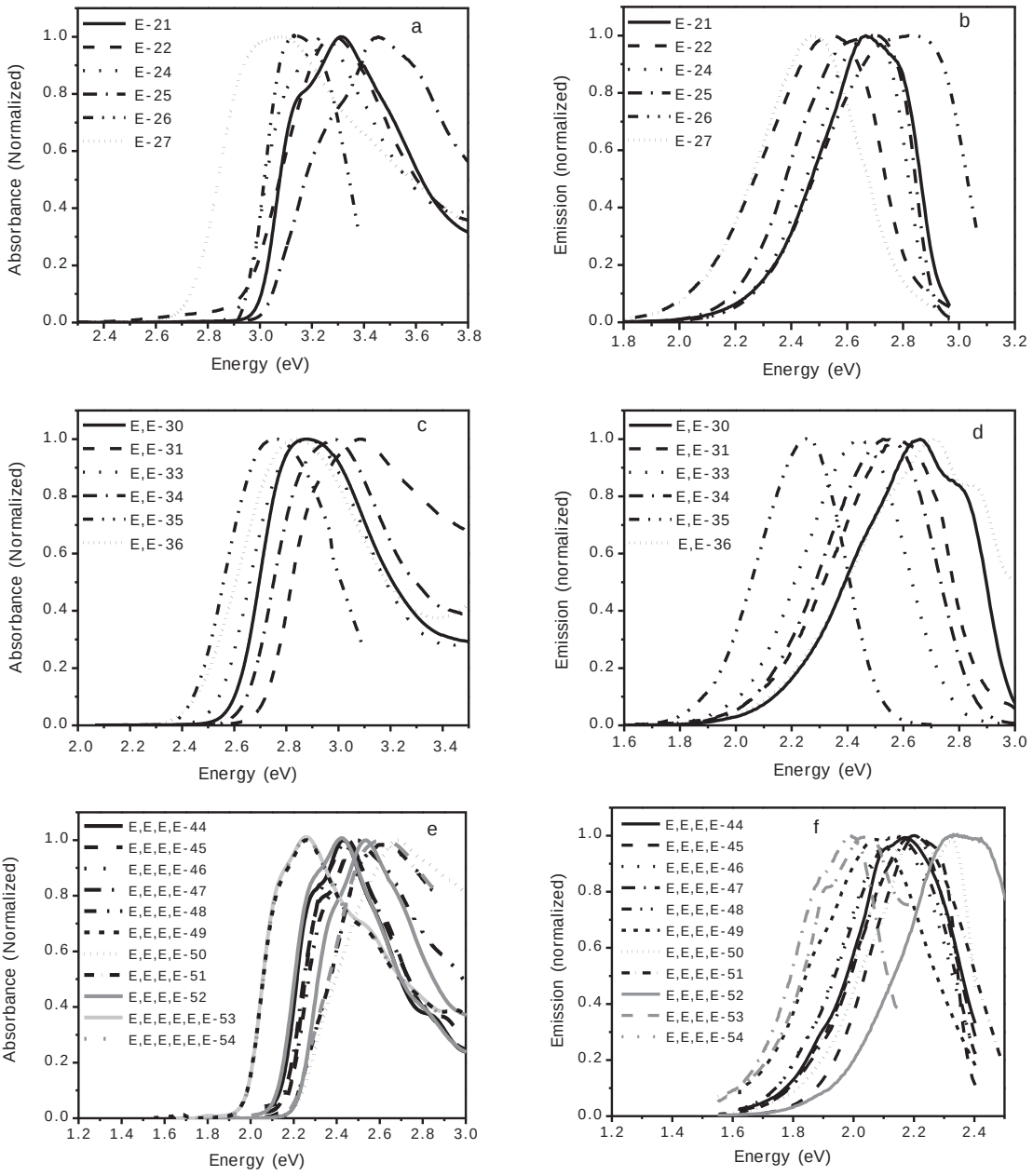


Figure 1. a) Normalized absorption spectra of protected di-arylenevinylene **E-21–E-27**. b) Normalized emission spectra of protected di-arylenevinylene **E-21**–**E-27**. c) Normalized absorption spectra of deprotected diarylenevinylene **E-30**–**E-36**. d) Normalized emission spectrum of deprotected diarylenevinylene **E-30**–**E-36**. e) Normalized absorption spectra of penta-arylenevinylene **E,E,E,E-44**–**E,E,E,E-52** and hepta-arylenevinylene **E,E,E,E,E,E-53**–**E,E,E,E,E,E-54**. f) Normalized emission spectra of penta-arylenevinylene **E,E,E,E-44**–**E,E,E,E-52** and hepta-arylenevinylene **E,E,E,E,E,E-53**–**E,E,E,E,E,E-54**.

the solvent was removed under reduced pressure, obtaining **17** in the form of brown oil (quant).

^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.84 (s, 1H), 6.01(s, 1H), 3.85(s, 4H), 1.29(m, 12H), 0.19 (t, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}) 180.0, 151.27, 140.98, 115.07, 105.21, 77.32, 34.13, 31.23, 26.7, 23.41, 14.31; MS (TOF LD+) *m/z*: 297 $[M+H]^+$.

3,3-Dibutyl-6-(5,5-dimethyl-1,3-dioxan-2-yl)-3,4-dihydro-2H-thieno[3,4-b][1,4] dioxpine, **18**: 2,2-methyl-1,3-propanediol (1.2 g, 11 mmol) and catalytic quantity of *p*-toluenesulfonic acid were added to a solution of **17** (2.37 g, 8 mmol) in toluene (50 mL). The reaction mixture was heated to reflux for 1 day then the solvent was removed under reduced pressure. The crude product was purified using column chromatography (alumina; 30% dichloromethane in hexane), yielding **18** as brown oil (quant.).

^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 6.15 (s, 1H), 5.60 (s, 1H), 3.88 (s, 4H), 3.57 (d, 2H), 3.45 (d, 2H), 1.12 (s, 3H), 1.29(m, 12H), 0. 19 (t, 6H), 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 149.97, 140.98, 115.07, 105.21, 99.01, 77.32, 34.13, 31.23, 30.09, 26.7, 23.41, 14.31; MS (TOF LD+) *m/z*: 383.22 $[M+H]^+$.

1-(3,3-Dibutyl-8-(5,5-dimethyl-1,3-dioxan-2-yl)-3,4-dihydro-2H-thieno[3,4-b][1,4] dioxepin-6-yl)-N,N-dimethylmethanamine, **19**: A solution of dimethylimminium chloride (0.36 g, 3.9 mmol) in acetonitrile (10 mL) was added slowly, to a solution of **18** (1 g, 2.6 mmol) in dichloromethane (20 mL) at room temperature and under an inert atmosphere. A white

Table 1. Electronic and optical properties of the different penta-arylenevinylenes and hepta-arylenevinylenes.

Material	HOMO Theoretical[a)] [eV]	LUMO Theoretical[a)] [eV]	HOMO [eV]	LUMO [eV]	Absorption (edge) [eV]	Absorption (max) [eV]	Emission (max) [eV]
E,E,E,E-44	4.16	2.01	4.45	2.19	2.14	2.42	2.10
E,E,E,E-45	4.27	2.12	4.58	2.30	2.16	2.47	2.19
E,E,E,E-46	4.35	2.09	4.19	3.15	2.12	2.42	2.07
E,E,E,E-47	4.24	2.04	4.48	2.10	2.15	2.45	2.20
E,E,E,E-48	4.30	2.09	4.11	1.91	2.18	2.50	2.14
E,E,E,E-49	3.97	1.80	4.33	3.07	2.22	2.54	2.25
E,E,E,E-50	4.30	2.15	4.53	2.31	2.23	2.52	2.20
E,E,E,E-51	4.35	2.18	4.59	2.35	2.21	2.53	2.25
E,E,E,E-52	4.27	2.07	5.17	3.1	2.21	2.57	2.19
E,E,E,E,E,E-53	4.13	2.28	4.49	2.89	2.00	2.25	2.02
E,E,E,E,E,E-54	4.10	2.23	5.01	3.07	2.00	2.26	1.99

[a)]Density functional theory (DFT) calculation B3LYP 6-31G.

precipitate formed, and then the solution was refluxed for an additional 1 h and cooled to room temperature. Et_3N (10 mL) were added to the solution and stirred for an additional 30 min at room temperature. The product was extracted from the reaction mixture with DCM, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was subsequently used as-is for the next step.

^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 6.15 (s, 1H), 3.88 (s, 4H), 3.57 (d, 2H), 3.45 (d, 2H), 2.25 (s, 6H), 1.12 (s, 3H), 1.29(m, 12H), 0. 19 (t, 6H), 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 149.97, 140.98, 115.07, 105.21, 99.01, 77.32, 51.98, 44.59, 34.13, 31.23, 30.09, 26.7, 23.41, 14.31; MS (TOF LD+) *m/z*: 440.27 $[M+H]^+$.

1-(3,3-Dibutyl-8-(5,5-dimethyl-1,3-dioxan-2-yl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-N,N,N-trimethyl-methanamineiodiode, ***20***: Excess of methyl iodide was added to a solution of **19** (330 mg, 0.75 mmol) in a mixture $CHCl_3$ (10 mL) and Et_2O (15 mL). After stirring the mixture for 12 h in the dark, the precipitate was filtered and washed with Et_2O, yielding ***20*** in the form of white crystals (quant).

^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 6.15 (s, 1H), 3.88 (s, 4H), 3.57 (d, 2H), 3.45 (d, 2H), 2.25 (s, 9H), 1.12 (s, 3H), 1.29(m, 12H), 0.19 (t, 6H), 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 149.97, 140.98, 115.07, 105.21, 99.01, 77.32, 55.98, 51.59, 34.13, 31.23, 30.09, 26.7, 23.41, 14.31; MS (TOF LD+) *m/z*: 582.71 $[M+H]^+$.

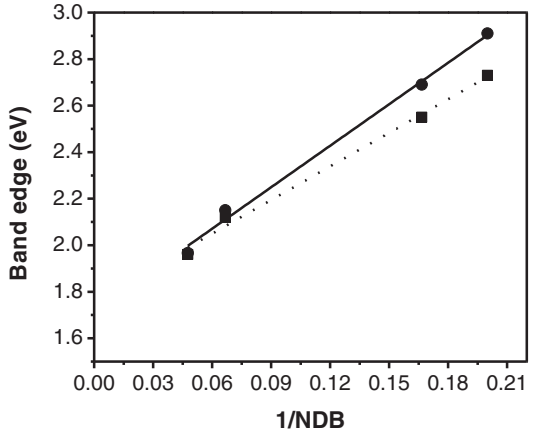


Figure 2. Energy of the absorption band edge as a function of 1/NDB (1/(number of double bonds)) of **E-27**, **E-36**, **E,E,E,E-50**, and **E,E,E,E,E,E-54** (•,–) and **E-22**, **E-31**, **E,E,E,E-45**, and **E,E,E,E,E,E-53** (■,···).

Diethyl(3,3-dibutyl-8-(5,5-dimethyl-1,3-dioxan-2-yl)-3,4-dihydro-2H-thieno[3,4-b][1,4] dioxepin-6-yl) methylphosphonate, ***9***: A solution of **20** in triethyl phosphite (10 mL) was stirred overnight at 150 °C under an inert atmosphere, and then cooled to room temperature. An excess of DMF and triethyl phosphite were removed under reduced pressure and water was added to the mixture. The crude product was extracted with Et_2O and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was washed with hexane in order to remove traces of triethyl phosphite. The product was purified by column chromatography (alumina; 100% DCM) yielding **9** in the form of a yellowish oil (quant).

^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 5.58 (s, 1H), 4.13 (s, 4H), 4.03 (m, 4H), 3.64 (d, 2H), 3.51 (d, 2H), 3.15 (s, 1H), 3.08 (s, 1H), 1.23 (t, 6H), 1.19 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 149.97, 140.98, 115.07, 105.21,99.01, 77.32, 60.01, 34.13, 31.23,30.09, 26.7, 23.41, 16.98, 14.39, 14.08; MS (TOF LD+) *m/z*: 533.25 $[M+H]^+$.

General Procedure for Preparation of Acetal Protected Di- and Tri-arylenevinylenes: All nine acetal protected di-arylenevinylenes as well as the two acetal protected tri-arylenevinylenes were prepared by coupling between the respective aldehydes and acetal protected bifunctional monomers **8** and **9**. All the reactions were performed using the same conditions: 1.1 eq. of the bifunctional monomer were dissolved in dry THF (15 mL) in a two necked flask and the reaction mixture cooled to –10 °C, under nitrogen atmosphere. 2 eq. of *t*-BuOK were then added to the solution turning its color into deep red. 1 eq. of a solution of the respective aldehyde in dry THF was added at –10 °C to the deep red solution and the resulting mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and water was added to the mixture. The product was extracted with DCM and the organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude was purified by column chromatography (alumina; 30% DCM in hexane) **E-21**–**E-29** and **E,E-39**–**E,E-40**.

The NMR spectra of the reaction mixtures showed that materials **E-21**–**E-29** and **E,E-39**–**E,E-40** (all in >90% of the **E** isomer) were obtained as the sole products and the reactions proceeded to completion.

5-(2-Ethylhexyl)-2,3-dihydro-7-((E)-2-(2,3-dihydro-5-(5,5-dimethyl-1,3-dioxan-2-yl)thieno[3,4-b][1,4]dioxin-7-yl)vinyl)thieno[3,4-b][1,4]dioxine, ***E-21***: Yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 6.89 (d, 1H), 6.74 (d, 1H), 5.64 (s, 1H), 4.19 (s, 8H), 3.69 (d, 2H), 3.60 (d, 2H), 2.54 (d, 2H), 1.53 (s, 1H), 1.25 (q, 11H), 0.85 (t, 6H). 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 138.98, 138.70, 138.27, 137.44, 117.50, 116.54, 115.82, 114.08 113.15, 110.73, 95.26, 64.81, 53.35, 40.44, 32.30, 31.82, 30.03, 29.74, 29.59, 29.26, 28.68, 25.51, 22.94, 22.74, 22.59, 21.69, 14.07, 14.04, 10.72; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{28}H_{38}O_6S_2$, 535.2109; found, 535.2178.

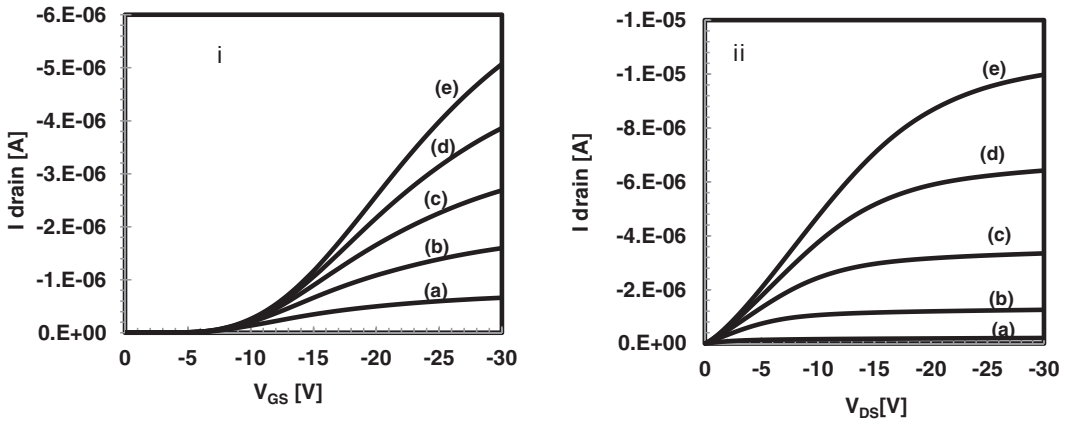


Figure 3. Electronic characterization of penta-arylenevinylene (E,E,E,E-50). i) Drain-source current as a function of the gate-source voltage (V_{GS}), for various values of the drain voltage (V_{DS}). a) –2 V; b) –4 V; c) –6 V; d) –8 V; e) –10 V. ii) Drain-source current as a function of V_{DS}, for various values of V_{GS}. a) 0 V; b) –5 V; c) –10 V; d) –15 V; e) –20 V.

3,3-Dibutyl-3,4-dihydro-6-((E)-2-(2,3-dihydro-5-(5,5-dimethyl-1,3-dioxan-2-yl)thieno[3,4-b][1,4]dioxin-7-yl)vinyl)-2H-thieno[3,4-b][1,4]dioxepine, ***E-22***: Yield: 94%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 6.97 (d, 1H), 6.83 (d, 1H), 6.78 (d, 1H), 6.63 (d, 1H), 5.69 (s, 1H), 4.23 (s, 4H), 3.73 (d, 2H), 3.64 (d, 2H), 2.77 (t, 2H), 1.68 (t, 2H), 1.39 (m, 6H), 1.29 (s, 3H), 0.90 (t, 3H), 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 145.05, 140.42, 138.99, 137.99, 125.61, 124.50, 120.39, 116.66, 116.35, 111.43, 95.21, 64.79, 31.49, 31.40, 30.01, 3.00, 28.65, 22.76, 22.49, 21.70, 14.03; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{32}O_4S_2$, 549.2266; found, 549.2798.

5-(3,4,5-Trimethoxystyryl)-2,3-dihydro-7-(5,5-dimethyl-1,3-dioxan-2-yl) thieno[3,4-b] [1,4]dioxine, ***E-23***: Yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.32 (d, 2H), 6.95 (d, 1H), 6.60 (d, 1H), 6.58 (d, 2H), 5.70 (s, 1H), 4.20 (s, 4H), 3.72 (d, 2H), 3.64 (d, 2H), 3.27 (t, 4H), 1.57 (q, 4H), 1.31 (t, 3H), 0.97 (t, 6H), 0.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 147.52, 139.09, 137.06, 127.39, 127.02, 124.35, 118.08, 122.94, 111.57, 110.15, 95.36, 64.88, 64.64, 50.68, 30.05, 29.42, 22.83, 21.73, 20.28 14.00; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{30}H_{43}NO_4S$, 486.2599; found, 486.3019.

4-((E)-2-(2,3-Dihydro-5-(5,5-dimethyl-1,3-dioxan-2-yl)thieno[3,4-b][1,4] dioxin-7-yl) inyl)-N,N-diphenylbenzenamine, ***E-24***: Yield: 92%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.57 (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 (75 MHz, $CDCl_3$, $<\delta_{ppm}$): 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; MS (TOF LD+) *m/z*: 526.19 $[M+H]^+$.

9-Hexyl-3-((E)-2-(2,3-dihydro-5-(5,5-dimethyl-1,3-dioxan-2-yl) thieno[3,4-b][1,4]dioxin-7-yl)vinyl)-9H-carbazole, ***E-25***: Yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 8.13 (d, 2H), 7.57 (d, 1H), 7.54 (m, 4H), 7.12 (d, 1H), 7.11 (d, 1H), 5.69 (s, 1H), 4.26 (s, 4H), 4.20 (d, 2H), 3,72 (d, 2H), 3.64 (d, 2H), 1.83 (m, 2H), 1.42 (q, 8H), 1.29 (s, 3H), 0.85 (t, 3H). 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 140.70, 139.97, 139.04, 137.58, 128.35, 127.71, 124.16, 123.05, 122.74, 118.82, 118.13, 117.68, 115.17, 110.86, 108.72, 95.33, 64.81, 53.35, 44.44, 31.50, 31.47, 30.08, 26.85, 22.57, 22.45, 22.30; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{33}H_{41}NO_4S$, 532.2443; found, 532.2524.

N,N-Dibutyl-4-((E)-2-(2,3-dihydro-5-(5,5-dimethyl-1,3-dioxan-2-yl) thieno[3,4-b][1,4]dioxin-7-yl)vinyl)benzenamine, ***E-26***: Yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.02(d, 1H), 6.78 (d, 1H), 6.63 (d, 2H), 5.67(s, 1H), 4.24 (s, 4H), 3.85 (d, 9H), 3.70 (d, 2H), 3.62 (d, 2H), 1.26 (s, 3H). 0.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 153.19, 138.97, 138.27, 137.48, 132.93, 126.33, 117.28, 116.57, 111.91, 102.98, 95.09, 64.74, 64.67, 55.89, 29.99 22.70, 21.63; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{28}O_7S$, 449.1555; found, 449.1650.

5-((E)-2-(5-Hexylthiophen-2-yl)vinyl)-2,3-dihydro-7-(5,5-dimethyl-1,3-dioxan-2-yl)thieno[3,4-b][1,4]dioxine, ***E-27***: Yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 6.97 (d, 1H), 6.83 (d, 1H), 6.78 (d, 1H), 6.63 (d, 1H), 5.69 (s, 1H), 4.23 (s, 4H), 3.73 (d, 2H), 3.64 (d,2H), 2.77 (t, 2H), 1.68 (t, 2H), 1.39 (m 6H), 1.29 (s, 3H), 0.90 (t, 3H), 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 145,05, 140.42, 138.99, 137.99, 125.61, 124.50, 120.39, 116.66, 116.35, 111.43, 95.21, 64.79, 31.49, 31.40, 30.01, 3.00, 28.65, 22.76, 22.49, 21.70, 14.03; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{32}O_4S_2$, 449.1742; found, 449.1798.

3,3-Dibutyl-6-((E)-2-(5-hexylthiophen-2-yl)vinyl)-3,4-dihydro-8-(5,5-dimethyl-1,3-dioxan-2-yl)-2H-thieno[3,4-b][1,4]dioxepine, ***E-28***: Yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.57 (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), 1.21(m, 12H), 1.15 (s, 3H), 0.72 (s, 9H); ^{13}C NMR (75 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, 77.79,.31.49, 31.40, 30.01, 28.65, 24.7, 23.6, 22.76, 22.49, 21.70, 14.03; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{41}H_{49}O_4S_2$, 652.3382, found, 652.3289.

N-(4-((E)-2-(3,3-Dibutyl-3,4-dihydro-6-(5,5-dimethyl-1,3-dioxan-2-yl)-2H-thieno[3,4-b][1,4]dioxepin-8-yl)vinyl)phenyl)-N-phenylbenzenamine, ***E-29***: Yield 92%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 6.98 (d, 1H), 6.93 (d, 1H), 6.78 (d, 1H), 6.63 (d, 1H), 5.69 (s, 1H), 4.23 (s, 4H), 3.73 (d, 2H), 3.64 (d,2H), 2.77 (t, 2H), 1.68 (t, 2H), 1.39 (m 6H), 1.29 (s, 7H), 0.90 (t, 11H), 0.70 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 149,05, 145.42, 139.98, 138.09, 126.51, 124.98, 121.39, 117.36, 116.75, 111.43, 95.21, 77.79, 77.4, 31.49, 31.40, 30.01, 3.00, 28.65, 22.76, 22.49, 21.70, 14.03; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{33}H_{50}O_4S_2$, 575.3150; found, 575.3298.

6-[(E)-2-[5-[(E)-2-[5-(5,5-Dimethyl-1,3-dioxan-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl]vinyl]-2,3-dihydrothieno[3,4-b][1,4] dioxin-7-yl]vinyl]-3,3-dibutyl-2,4-dihydrothieno [3,4-b][1,4]dioxepine, ***E,E-39***: Yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 6.97(d, 2H), 6.63 (s, 2H), 6.01(s, 1H), 5.63 (s, 1H), 4.21 (t, 18H), 3.87 (s, 2H), 3.81 (s, 2H), 3.69 (d, 2H), 3.61 (d,2H), 1.33 (t, 12H), 1.25 (t, 3H), 0.93 (t, 6H). 0.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 147.98, 146.82, 138.95 137.82, 128.01, 120.99, 120.01, 114.02, 114.12, 104.11, 65.78, 64.43, 44.23, 43.89, 32.43, 31.98, 29.76, 29.01, 24.78, 23.39, 22.58, 21.71, 14.03, 13.93; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{37}H_{46}O_8S_3$, 715.2354; found, 715.9531.

5-(5,5-Dimethyl-1,3-dioxan-2-yl)-7-[(E)-2-[7-[(E)-2-(5-hexyl-2-thienyl) vinyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl]vinyl]-2,3-dihydrothieno[3,4-b] [1,4]dioxine, ***E,E-40***: Yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.01 (d, 1H), 6.91 (d, 1H), 6.78 (d, 2H), 6.63 (d, 2H), 5.69 (s, 1H), 4.23 (t, 8H), 3.73 (d, 2H), 3.64 (d, 2H), 2.77 (t, 2H), 1.68 (t, 2H), 1.39 (m, 6H),

1.29 (s, 3H), 0.90 (t, 3H), 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 146,91, 141.39, 139.86, 138.09, 126.76, 124.50, 120.39, 116.66, 116.35, 111.43, 95.21, 64.79, 31.49, 31.40, 30.01, 3.00, 28.65, 22.76, 22.49, 21.70, 14.03; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{32}H_{38}O_6S_3$, 615.1830; found, 615.8456.

General Procedure for Deprotection of Acetal Protected Di- and Tri-arylenevinylenes: Acetal protected di- and tri-arylenevinylenes (**E-21**–**E-29** and **E,E-39**–**E,E-40**) were dissolved in a mixture of THF (10 mL) and 1:1 37% aqueous HCl and water (10 mL) and stirred for 1 h at room temperature. The solution was then neutralized and the product extracted with DCM. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The products **E-30**–**E-38** and **E,E-41**–**E,E-42** were purified using column chromatography (silica, 50% DCM in hexane). The NMR spectra of the reaction mixtures showed that materials **E-30**–**E-38** and **E,E-41**–**E,E-42** (all in >95% of the **E** isomer) were obtained as the sole products and the reactions proceeded to completion.

7-((E)-2-(5-(2-Ethylhexyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)vinyl)-2,3-di hydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde, ***E-30***: Yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.84 (s, 1H), 7.15 (d, 1H), 6.73 (d, 1H), 4.32 (s, 8H), 2.55 (d, 2H), 1.53 (s, 1H), 1.25 (q, 8H), 0.85 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 178.93, 140.47, 138.46, 137.58, 129.39, 121.56, 118.87, 114.40, 113.09, 112.59, 65.27, 64.41, 40.42, 32.31, 29.91, 28.66, 25.53, 22.91, 14.04, 10.70; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{28}O_5S_2$, 449.1378; found, 449.1456.

7-((E)-2-(3,3-Dibutyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl) vinyl)-2,3-dihydrothieno3,4-b][1,4]dioxine-5-carbaldehyde, ***E-31***: Yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.78 (s, 1H), 7.17 (d, 1H), 6.76 (d, 1H), 6.31 (s, 1H), 5.58 (s, 1H), 4.13 (s, 4H), 3.88 (s, 2H), 3.79 (s, 2H), 1.33 (t, 12H), 0.88 (m, 6H);^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 179.31, 148.42, 147.18, 139.59 138.12, 128.42, 121.59, 120.43, 114.81, 114.07, 104.02, 65.27, 64.43, 43.53, 43.51, 31.80, 31.45, 29.58, 29.54, 29.24, 24.88, 23.40, 22.58, 14.03, 13.93; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{30}O_5S_2$, 463.1534; found, 463.1636.

7-(4-(Dibutylamino)styryl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde, ***E-32***: Yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.82 (s, 1H), 7.32 (d, 2H), 6.95 (d, 1H), 6.60 (d, 1H), 6.58 (d, 2H), 5.70 (s, 1H), 4.20 (s, 4H), 3.72 (d, 2H), 3.64 (d, 2H), 3.27 (t, 4H), 1.57 (q, 4H), 1.35 (t, 4H), 0.94 (t, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 178.85, 148.42, 137.09, 132.06, 130.39, 128.34, 123.05, 113.90, 111.81, 111.38, 110.15, 95.36, 64.88, 64.64, 29.33, 20.21, 13.89; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{29}H_{43}NO_3S$, 399.1868; found, 399.5462; mp = 112 °C.

7-(4-(Diphenylamino)styryl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde, ***E-33***: Yield: 98%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.87 (s, 1H), 7.80 (d, 2H), 7.3 (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 (75 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; MS (TOF LD+) *m/z*: $C_{27}H_{21}NO_3S$, 440.12 $[M+H]^+$.

7-((E)-2-(9-Hexyl-9H-carbazol-6-yl)vinyl)-2,3-dihydrothieno[3,4-b][1,4] dioxine-5-carbaldehyde, ***E-34***: Yield: 96%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.89 (s, 1H), 8.13 (d, 2H), 7.57 (d, 1H), 7.54 (m, 4H), 7.12 (d, 1H), 7.11 (d, 1H), 5.69 (s, 1H), 4.26 (s, 4H), 4.20 (t, 2H), 1.83 (m, 2H), 1.42 (q, 8H), 0.83 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 178.97, 148.92, 140.70,140.65, 140.57, 137.87, 132.81, 129.27, 127.16, 125.90, 123.07, 122.80, 122.61, 119.17, 114.40, 114.29, 108.90, 64.81, 53.35, 42.97, 31.46, 31.45, 30.79, 28.82, 26.81, 22.49, 13.96; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{27}H_{27}NO_3S$, 446.1711; found, 446.1791.

7-(3,4,5-Trimethoxystyryl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde, ***E-35***: Yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.87 (s, 1H), 7.02 (s, 2H), 6.78 (d, 1H), 6.58 (d, 1H), 4.24 (s, 4H). 3.89 (d, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 179.36, 153.19, 148.76, 138.67, 138.60, 131.93, 131.59, 127.97, 116.67, 115.37, 103.86, 64.74, 64.67, 60.94, 56.13; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{18}O_6S$, 363.0824; found, 363.0798.

7-((E)-2-(5-Hexylthiophen-2-yl)vinyl)-2,3-dihydrothieno[3,4-b][1,4] dioxine-5-carbaldehyde, ***E-36***: Yield: 96%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.84 (s, 1H), 7.23 (d, 1H), 6.89 (d, 1H), 6.79 (s, 1H), 6.64 (s, 1H), 4.13 (s, 4H), 2.71 (t,2H), 1.65 (t, 2H), 1.29 (m, 6H), 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 179.11, 148.12, 147.38, 139.39 138.15, 128,15, 127.95, 125.25, 124.94, 115.38, 114.91, 65.26, 64.44, 31.44, 31.30, 30.37, 28.62, 22.45, 13.98; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{19}H_{22}O_3S_2$, 363.1010; found, 363.1074.

8-(4-(Diphenylamino)styryl)-3,3-dibutyl-3,4-dihydro-2H-thieno[3,4-b][1,4] dioxepine-6-carbaldehyde, ***E-37***: Yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.91(s, 1H), 7.57 (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), 1.21(m, 12H),1.15 (s, 3H), 0.72 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 179.01, 148.93, 147.01, 142.02, 138.82, 136.08, 132.97, 132.04, 130.01, 128.17, 127.1, 126.4, 126.03, 125.2, 125.03, 124.94, 124.08, 118.2, 113.8, 97.2, 79.5, 77.79,.31.49, 31.40, 30.01, 28.65, 24.7, 23.6, 22.49, 21.70, 14.03; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{36}H_{39}NO_3S_2$, 566.2650; found, 566.2689.

3,3-Dibutyl-8-((E)-2-(5-hexylthiophen-2-yl)vinyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6-carbaldehydecarbaldehyde, ***E-38***: Yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.86 (s, 1H), 6.98 (d, 1H), 6.93 (d, 1H), 6.78 (d, 1H), 6.63 (d, 1H), 5.69 (s, 1H), 4.23 (s, 4H), 2.77 (t, 2H), 1.68 (t, 2H), 1.39 (m, 6H), 1.29 (s, 7H), 0.90 (t, 11H), 0.70 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 178.98, 148,05, 143.92, 140.18, 139.10, 129.95, 127.38, 122.39, 118.96, 117.63, 111.93, 96.21, 77.4, 31.09, 30.01, 3.00, 28.65, 24.96, 23.79, 21.89, 14.13; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{28}H_{40}O_3S_2$, 489.2418; found, 489.2349.

7-[(E)-2-[7-[(E)-2-(3,3-Dibutyl-2,4-dihydrothieno[3,4-b][1,4]dioxepin-6-yl) vinyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl]vinyl]-2,3-dihydrothieno[3,4-b] [1,4]dioxine-5-carbaldehyde, ***E,E-41***: Yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.81 (s, 1H), 7.19 (d, 1H), 6.80 (d, 1H), 6.39 (s, 1H), 5.58 (s, 1H), 4.13 (s, 8H), 3.88 (s, 2H), 3.79 (s, 2H), 1.33 (t, 12H), 0.88 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 179.31, 148.42, 147.18, 139.59 138.12, 128.42, 121.59, 120.43, 114.81, 114.07, 104.02, 65.27, 64.43, 43.53, 43.51, 31.80, 31.45, 29.58, 29.54, 29.24, 24.88, 23.40, 22.58, 14.03, 13.93; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{32}H_{36}O_7S_3$, 629.1623; found, 628.8243.

7-[(E)-2-[7-[(E)-2-(5-Hexyl-2-thienyl)vinyl]-2,3-dihydrothieno[3,4-b][1,4] dioxin-5-yl]vinyl]-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde, ***E,E-42***: Yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 9.79 (s, 1H), 7.43 (d, 1H), 6.81 (d, 1H), 6.73 (s, 1H), 6.64 (s, 1H), 4.13 (s, 8H), 2.71 (t, 2H), 1.65 (t, 2H), 1.29 (m, 6H), 0.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 180.01, 149.01, 148.32, 140.13, 138.95, 128,79, 128.25, 125.84, 125.04, 116.18, 114.91, 65.26, 64.44, 31.44, 31.30, 30.37, 28.62, 22.45, 13.98; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{28}O_5S_3$,529.1098; found, 529.7641.

General Procedure for the Preparation of Penta- and Hepta-arylenevinylenes: *t*-BuOK (4 eq.) was added to a solution of bifunctional monomer **43**[27] (1 eq.) in dry THF under nitrogen atmosphere and at –10°C, turning the solution deep red. 2.1 eq. of the respective deprotected aldehyde (**E-30**–**E-38** and **E,E-41**–**E,E-42**) were then added to the solution and the resulting mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure, and then water and DCM were added to the crude. The organic phase was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The products (**E,E,E,E-44**–**E,E,E,E-52** and **E,E,E,E,E-53**–**E,E,E,E,E-54**) were purified by column chromatography (alumina, 0–30% DCM in hexane). The NMR spectra of the reaction mixtures showed that materials **E,E,E,E-44**–**E,E,E,E-52** and **E,E,E,E,E-53**–**E,E,E,E,E-54** (all in >80% of the **E** isomer) were obtained as the sole products.

5-((1E)-2-(5-((1E)-2-(2,5-Bis(2-ethylhexyloxy)-4-((1E)-2-(5-((E)-2-(5-(2-ethylhexyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl) vinyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)vinyl)phenyl) vinyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)vinyl)-7-(2-ethylhexyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine, ***E,E,E,E-44***: Yield: 89%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.19 (d, 2H), 7.14 (d, 2H), 6.97 (d, 2H), 6.87 (d, 4H), 4.27 (s, 8H), 3.91 (d, 4H), 3.84 (d, 4H), 2.51 (d, 4H), 1.85 (t, 2H), 1.54 (t, 4H), 1.39 (m, 32H), 0.80 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 150.95, 139.18, 138.60, 138.59, 138.31, 132.32, 130.78, 128.69, 126.31, 116.09, 115.97, 115.93, 113.62, 71.55, 68.03, 64.76, 40.46, 39.70, 32.33, 31.82, 30.78, 30.24, 29.60, 29.56, 29.26, 29.19, 28.81, 28.70, 25.54, 24.08, 23.62, 23.04, 22.94, 22.88, 22.59, 14.08, 14.06, 14.02, 11.28, 10.85,0.91; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{70}H_{94}O_{10}S_4$, 1223.5721; found, 1223.5763.

6-((1E)-2-(5-((1E)-2-(2,5-Bis(2-ethylhexyloxy)-4-((1E)-2-(5-((E)-2-(3,3-dibutyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)vinyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)vinyl)phenyl)vinyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)vinyl)-3,3-dibutyl-3,4-dihydro-2H-thieno[3,4-b][1,4] dioxepine, ***E,E,E,E-45***: Yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.19 (d, 2H), 7.14 (d, 2H), 6.97 (d, 2H), 6.87 (d, 4H), 6.25 (s, 2H), 4.27 (s, 8H), 3.91 (d, 8H), 3.84 (d, 4H), 1.54 (t, 2H), 1.39 (m, 40H), 0.80 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 141.51, 139.18, 139.14, 126.32, 121.82, 121.16, 117.74, 116.52, 116.30, 115.61, 115.16, 109.71, 101.80, 71.58, 64.80, 43.58, 43.55, 39.77, 31.46, 31,42, 30.80, 29.62, 29.33, 24.12, 23.48, 23.08, 23.04, 22.58, 14.03, 13.93; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{72}H_{98}O_{10}S_4$, 1251.6042; found, 1251.4038.

(1E,2E)-1-((2Z)-3-((3E)-4-(2,5-Bis(2-ethylhexyloxy)-4-((1E)-2-(5-(4-(dibutylamino)styryl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)vinyl)phenyl) but-3-en-2-ylidene)-1,4-dioxan-2-ylidene)-3-(4-(dibutylamino)phenyl)prop-2-ene-1-thiol, ***E,E,E,E-46***: Yield: 85%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.23 (d, 4H), 7.18 (d, 4H), 7.07 (d, 2H), 6.95 (d, 4H), 6.69 (d, 2H), 6.58 (d, 4H), 4.27 (s, 8H), 3.92 (d, 4H), 3.26 (t, 8H), 1.81 (m, 2H), 1.57-1.38 (m, 32H), 0.94 (t, 24H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 150.94, 147.46, 139.22, 138.11, 127.39, 126.66, 126.32, 124.35, 120.47, 117.65, 116.71, 115.24, 112.91, 111.52, 109.60, 71.62, 64.88, 64.64, 50.68, 39.74, 30.81, 29.42, 29.22, 24.10, 23.07, 20.26, 14.14, 14.05, 13.93, 11.33; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{71}H_{100}N_2O_6S_2$, 1125.6709; found, 1125.7060.

4-((1E)-2-(5-(2,5-Bis(2-ethylhexyloxy)-4-((1E)-2-(5-(4-(diphenylamino) styryl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)vinyl)styryl)-2,3-dihydrothieno-[3,4-b][1,4]dioxin-7-yl)vinyl)-N,N-diphenyl benzenamine, ***E,E,E,E-47***: Yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 8.18(d, 4H), 7.62(d, 2H), 7.60 (m, 8H), 7.24(d, 8H), 7.04(d, 2H), 4.26(s, 8H), 4.20(t, 4H), 3.944(d, 4H), 1.83 (m, 6H), 1.61 (q, 4H), 1.47(m, 28H), 1.01(m, 12H), 0.87(t, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 151.01, 145.07, 140.73, 139.19, 139.16, 128.52, 126.35, 125.48, 124.60, 121.14, 116.51, 115.24, 109.60, 71.55, 64.80, 39.77, 31.54, 31.42, 30.85, 30.37, 29.66, 29.26, 28.72, 24.14, 23.11, 22.54, 14.17, 14.05, 11.36; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{78}H_{80}N_2O_6S_2$, 1205.5457; found, 1205.3567.

2-((1E)-2-(5-((1E)-2-(2,5-Bis(2-ethylhexyloxy)-4-((1E)-2-(5-((E)-2-(9-hexyl-9H-carbozol-2-yl)vinyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)vinyl) phenyl)vinyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)vinyl)-9-hexyl-9H-carbazole, ***E,E,E,E-48***: Yield: 85%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 8.18 (d, 4H), 7.62 (d, 2H), 7.60 (m, 8H), 7.24 (d, 8H), 7.04 (d, 2H), 4.26 (s, 8H), 4.20 (t, 4H), 3.944 (d, 4H), 1.83 (m, 6H), 1.61 (q, 4H), 1.47 (m, 28H), 1.01 (m, 12H), 0.87 (t, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 151.01, 145.07, 140.73, 139.19, 139.16, 128.52, 126.35, 125.48, 124.60, 121.14, 116.51, 115.24, 109.60, 71.55, 64.80, 39.77, 31.54, 31.42, 30.85, 30.37, 29.66, 29.26, 28.72, 24.14, 23.11, 22.54, 14.17, 14.05, 11.36; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{78}H_{92}N_2O_6S_2$, 1217.6396; found, 1217.5446.

(1E,2E)-1-((2Z)-3-((3E)-4-(2,5-Bis(2-ethylhexyloxy)-4-((1E)-2-(5-(3,4,5-trimethoxystyryl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)vinyl)phenyl) but-3-en-2-ylidene)-1,4-dioxan-2-ylidene)-3-(3,4,5-trimethoxyphenyl)prop-2-ene-1-thiol, ***E,E,E,E-49***: Yield: 83%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.23 (s, 2H), 6.97 (d, 4H), 6.78 (d, 4H), 6.78 (d, 4H), 6.19 (s, 2H), 4.24 (s, 8H). 3.89 (m, 22H), 1.82 (m, 2H), 1.23 (m, 16H), 0.85 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 151.24, 148.76, 138.28, 136.11, 128.37, 126.66, 126.32, 124.55, 120.47, 117.65, 116.71, 115.24, 112.91, 111.52, 109.60, 71.62, 64.88, 64.64, 50.68, 56.06, 39.74, 30.81, 29.42, 29.22, 24.10, 23.07, 20.26, 14.14, 13.93, 11.33; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{61}H_{78}O_{12}S_2$, 1067.4925; found, 1067.5809 $(M+H^+)$.

5-(2,5-Bis(2-ethylhexyloxy)-4-((1E)-2-(5-((E)-2-(5-hexylthiophen-2-yl) vinyl)-2,3-dihy drothieno[3,4-b][1,4]dioxin-7-yl)vinyl)styryl)-7-((E)-2-(5-hexylthiophen-2-yl)vinyl)-2,3-dihy drothieno[3,4-][1,4]dioxine, ***E,E,E,E-50***: Yield: 91%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.17 (d, 4H), 6.97 (d, 2H), 6.83 (d, 4H), 6.77 (d, 2H), 6.60 (d, 2H), 4.27 (s, 8H), 3.90 (d, 4H), 2.71 (t, 4H), 1.54 (t, 4H), 1.29 (m, 28H), 0.80 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 151.01, 145.02, 140.73, 139.19 139.05, 126.35, 125.48, 124.60, 121.14, 119.90, 117.62, 116.51, 116.38, 115.24, 109.60, 71.55, 64.80 39.77, 31.54, 31,42, 30.37, 30.11, 29.66, 29.62, 29.33, 29.26, 28.72, 24.14, 23.11, 22.65, 22.54, 14.17, 14.05, 11.36; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{62}H_{82}O_6S_4$,1051.4994; found, 1051.5013.

N-(4-((1E)-2-(6-(4-((1E)-2-(6-(4-(Diphenylamino)styryl)-3,3-dibutyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-8-yl)vinyl)-2,5-bis(octan-3-yloxy) styryl)-3,3-dibutyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-8-yl)vinyl) phenyl)-N-phenylbenzenamine, ***E,E,E,E-51***: Yield: 88%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 77.62 (d, 4H), 7.60 (m, 16H), 7.24 (m, 16H), 6.95 (d, 4H), 4.26 (s, 8H), 4.20 (t, 4H), 3.92 (s, 4H), 1.81 (m, 2H), 1.21 (m, 40H), 1.15 (s, 6H), 0.72 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 178.01, 149.98, 148.21, 145.62, 139.81, 136.08, 133.91, 132.84, 131.01, 128.97, 127.62, 126.54, 126.21, 125.82, 125.03, 124.94, 124.08, 118.2, 113.8, 97.2, 79.5, 77.79,.31.49, 31.40, 30.01, 28.65, 24.7, 23.6, 22.49, 21.70, 14.03; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{96}H_{116}N_2O_6S_2$, 1457.8274; found, 1457.8189.

6-(4-((1E)-2-(3,3-Dibutyl-6-((E)-2-(5-hexylthiophen-2-yl)vinyl)-3,4-dihydro-2H-thieno[3,4-b]1,4]dioxepin-8-yl)vinyl)-2,5-bis(octan-3-yloxy)styryl)-3,3-dibutyl-8-((E)-2-(5-hexyl thiophen-2-yl)vinyl)-3,4-dihydro-2H-thieno[3,4-b] [1,4]dioxepine, ***E,E,E,E-52***: Yield: 87%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.27 (d, 4H), 6.99 (d, 2H), 6.83 (d, 4H), 6.77 (d, 2H), 6.60 (d, 2H), 4.3 (s, 8H), 3.92 (d, 4H), 2.71 (t, 4H), 1.81 (m, 2H), 1.54 (t, 4H), 1.29 (m, 28H), 1.19 (m, 24H), 0.80 (m, 30H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 151.01, 145.02, 140.73, 139.19 139.05, 126.35, 125.48, 124.60, 121.14, 119.90, 117.62, 116.51, 116.38, 115.24, 109.60, 71.55, 64.80 39.77, 31.54, 31,42, 30.37, 30.11, 29.66, 29.62, 29.33, 29.26, 28.72, 24.14, 23.11, 22.65, 22.54, 14.17, 14.05, 11.36; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{80}H_{118}O_6S_4$, 1303.7811; found, 1303.7853.

6-[(E)-2-[5-[(E)-2-[7-[(E)-2-[4-[(E)-2-[5-[(E)-2-[7-[(E)-2-(3,3-Dimethyl-2,4-dihydrothieno[3,4-b][1,4]dioxepin-6-yl)vinyl]-2,3-dihydrothieno[3,4-b][1,4] dioxin-5-yl]vinyl]-2,3-di hydrothieno[3,4-b][1,4]dioxin-7-yl]vinyl]-2,5-bis(2-ethylhexoxy)phenyl]vinyl]-2,3-dihydroth ieno[3,4-b][1,4]dioxin-5-yl]vinyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl]vinyl]-3,3-dimethyl-2,4-dihydrothieno[3,4-b][1,4]dioxepine, ***E,E,E,E,E,E-53***: Yield: 86%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.19 (d, 2H), 7.04 (d, 4H), 6.97 (d, 4H), 6.87 (d, 4H), 6.25 (s, 2H), 4.27 (s, 8H), 3.91 (d, 16H), 3.84 (d, 4H), 1.54 (t, 2H), 1.39 (m, 40H), 0.80 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 141.51, 139.18, 139.14, 126.32, 121.82, 121.16, 117.74, 116.52, 116.30, 115.61, 115.16, 109.71, 101.80, 71.58, 64.80, 43.58, 43.55, 39.77, 31.46, 31,42, 30.80, 29.62, 29.33, 24.12, 23.48, 23.08, 23.04, 22.58, 14.03, 13.93; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{88}H_{110}O_{14}S_6$, 1584.6219; found, 1584.6238.

5-[(E)-2-[7-[(E)-2-[2,5-Bis(2-ethylhexoxy)-4-[(E)-2-[5-[(E)-2-[7-[(E)-2-(5-methyl-2-thienyl)vinyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl]vinyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl]vinyl]phenyl]vinyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl]vinyl]-7-[(E)-2-(5-methyl-2-thienyl) vinyl]-2,3-dihydrothieno[3,4-b][1,4]dioxine, ***E,E,E,E,E,E-54***: Yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}): 7.19 (d, 4H), 6.89 (d, 2H), 6.80 (d, 4H), 6.77 (d, 4H), 6.60 (d, 4H), 4.27 (s, 16H), 3.90 (d, 4H), 2.71 (t, 4H), 1.54 (t, 4H), 1.29 (m, 28H), 0.80 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$, δ_{ppm}): 151.01, 145.02, 140.73, 139.19 139.05, 126.35, 125.48, 124.60, 121.14, 119.90, 117.62, 116.51, 116.38, 115.24, 109.60, 71.55, 64.80 39.77, 31.54, 31,42, 30.37, 30.11, 29.66, 29.62, 29.33, 29.26, 28.72, 24.14, 23.11, 22.65, 22.54, 14.17, 14.05, 11.36; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{78}H_{94}O_{10}S_6$, 1383.5171; found, 1383.9637.

Acknowledgements

The authors thank the European Community Marie Curie Actions, Marie Curie Research Training Network (BIMORE, Project No.: 35859, grant agreement No: 2008206) and the Technion Funds for Security Research. This article was amended on April 10, 2012 to correct an error in the spelling of author K. N. Shivananda's name that was present in the version originally published online.

Received: August 13, 2011
Published online: January 31, 2012

[1] a) K. Müllen, U. Scherf, *Organic Light Emitting Devices*, Wiley-VCH, Weinheim **2006**; b) T. Yokozawa, A. Yokoyama, *Chem. Rev.* **2009**, *109*, 5595.

[2] D. W. Samuel, G. A. Turnbull, *Chem. Rev.* **2007**, *107*, 1272.
[3] Z. Bao, J. Locklin, *Organic Field-Effect Transistors*, 1st ed., CRC Press, Boca Raton **2007**; b) C. D. Dimitropoulos, L. P. R. Malenfant, *Adv. Mater.* **2002**, *14*, 99.
[4] S. Ravishankar, B. Dudhea, S. Jasmine, A. Kumar, V. R. Rao, *Sens. Actuators B* **2010**, *148*, 158.
[5] a) C. Brabec, V. Dyakonov, U. Scherf, *Organic Photovoltaics; Materials, Device Physics, and Manufacturing Technologies*, Wiley-VCH, Weinheim **2008**; b) T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds, *Handbook of Conducting Polymers*, Marcel Dekker, New York, **1998**.
[6] H. Zhou, X. Zhao, T. Huang, R. Lu, H. Zhang, X. Qi, P. Xue, X. Liua, X. Zhang, *Org. Biomol. Chem.* **2011**, *9*, 1600.
[7] G. Barbarella, M. Melucci, G. Sotgiu, *Adv. Mater.* **2005**, *17*, 1581.
[8] 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.
[9] T. Maddux, W. Li, L. Yu, *J. Am. Chem. Soc.* **1997**, *119*, 844.
[10] M. Jorgensen, F. C. Krebs, *J. Org. Chem.* **2004**, *69*, 6688.
[11] A. Speicher, T. Backes, S. Grosse, *Tetrahedron* **2005**, *61*, 11692.
[12] T. Maddux, W. Li, L. Yu, *J. Am. Chem. Soc.* **1997**, *119*, 844.
[13] J. M. Tour, *J. Org. Chem.* **2005**, *70*, 3396.
[14] M. J. G. Escalonilla, F. Langa, J. M. Rueff, L. Oswaldb, J. F. Nierengarten, *Tetrahedron Lett.* **2002**, *43*, 7507.
[15] M. Jorgensen, F. C. Krebs, *J. Org. Chem.* **2004**, *69*, 6688.
[16] H. Noguchi, K. Hojo, M. Suginome, *J. Am. Chem. Soc.* **2007**, *129*, 758.
[17] a) O. Deeg, P. Kirsch, D. Pauluth, P. Bäuerle, *Chem. Commun.* **2002**, 2762; b) O. Deeg, P. Bäuerle, *Org. Biomol. Chem.* **2003**, *1*, 1609.
[18] a) C. A. Briehn, P. Bäuerle, *Chem. Commun.* **2001**, *40*, 4680; b) C. A. Briehn, P. Bäeuerle, *J. Comb. Chem.* **2002**, *4*, 457.
[19] S. Anderson, *Chem. Eur. J.* **2001**, *7*, 4706.
[20] 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.
[21] M. Firstenberg, K. N. Shivananda, I. Cohen, O. Solomeshch, V. Medvedev, N. Tessler, Y. Eichen, *Adv. Funct. Mater.* **2011**, *21*, 634.
[22] a) Y. Liang, B. Peng, J. Liang, Z. Tao, J. Chen, *Org. Lett.* **2010**, *12*, 1204; b) C. B. Thompson, Y. G. Kim, T. D. McCarley, J. R. Reynolds, *J. Am. Chem. Soc.* **2006**, *128*, 12714.
[23] M. Turbiez, P. Fre`re, J. Roncali, *J. Org. Chem.* **2003**, *68*, 5357.
[24] J. F. Morin, N. Drolet, Y. Tao, M. Leclerc, *Chem. Mater.* **2004**, *16*, 4619.
[25] G. Lai, X. R. Bu, J. Santos, E. A. Mintz, *Synlett.* **1997**, *11*, 1275.
[26] M. Jessing, M. Brandt, K. J. Jensen, J.B. Christensen, U. Boas, *J. Org. Chem.* **2006**, *71*, 6734.
[27] R. Koike, Y. Katayose, A. Ohta, J. Motoyoshiya, Y. Nishii, H. Aoyama, *Tetrahedron* **2005**, *61*, 11026.
[28] C. R. Newman, C. D. Frisbie, D. A. da Silva Filho, J. L. Brédas, P. C. Ewbank, K. R. Mann, *Chem. Mater.* **2004**, *16*, 4436.
[29] T. Mori, *J. Phys. Cond. Mater.* **2008**, *20*, 184010.
[30] 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*, 044.
[31] S. Shaked, S. Tal, Y. Roichman, A. Razin, S. Xiao, Y. Eichen, N. Tessler, *Adv. Mater.* **2003**, *15*, 913.
[32] a) D. M. Welsh, L. J. Kloeppner, L. Madrigal, M. R. Pinto, B. C. Thompson, K. S. Schanze, K. A. Abboud, D. Powell, J. R. Reynolds, *Macromolecules* **2002**, *35*, 6517; b) C. B. Nielsen, T. Bjørnholm, *Macromolecules* **2005**, *38*, 10379.