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SYNTHESIS OF *p*-PHENYLENE-VINYLENE-THIENYLENE OLIGOMERS

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Abstract- The preparation of alkoxylated phenylene-vinylene-thienylene oligomers with and without cyano substituents at the olefin moieties and their spectroscopic measurements are presented. Both thiophene ring and cyano groups may induce red shift in their absorption spectra.

INTRODUCTION

Poly-*p*-phenylenevinylenes (PPV) have been widely investigated as candidates for applications in electroluminescence (EL) devices.[1] Recently, we have reported the highly efficient blue-light electroluminescent material for light-emitting diodes (LED) from PPV type oligomers.[2] It shows that various functional groups placed at various positions in the molecule can indeed influence the photophysical property and the electroluminescent behavior of these materials in organic LED studies. Our preliminary results from ZINDO calculations[3] on our previous PPV type oligomers[2] and with thiophene ring to replace the phenylene moieties showed that thiophene ring could cause large red shifts in the absorption spectra.[4] Since thiophene oligomers have been continually attracted much attention to their biological activities[5] and as starting materials for the preparation of organic conductors.[6] The oligomers of similar structure such as α,α'-disubstituted di- and trithiophenes are also promising materials for many potential applications.[7] The presence of the alkoxylated phenylene-vinylene unit should enhance the solubility of oligomers compared with their thiophene

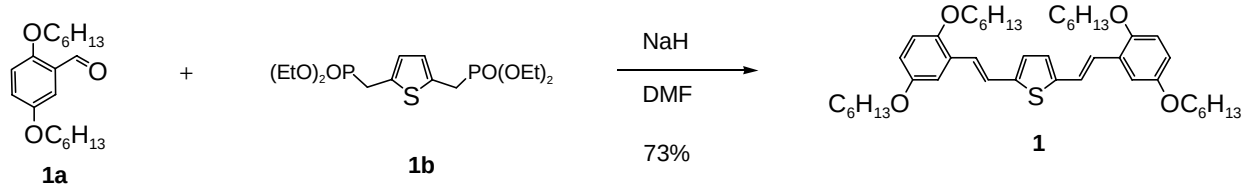
analogues. The introduction of high electron affinity cyano groups on the vinylene linkages of PPV derivatives has been reported to lower the energy of the LUMO and reduces the barrier to the electron injection in LED.[8] Thus, PPV derivatives containing cyano groups on the vinylene linkage present high electron affinity and therefore exhibit a relatively low threshold voltage and high quantum efficiency in LED devices even using stable aluminum electrodes.[9] However, despite the interesting properties in this field, as to our knowledge, there is no report in the literature about the synthesis of the thiophene oligomers containing with or without cyano groups on the vinylene linkage and with phenylene-vinylene groups capped at their α-positions.[10-16] Thus, in this paper, we wish to report the efficient synthesis and their spectroscopic characterizations of these oligomers.

RESULTS AND DISCUSSION

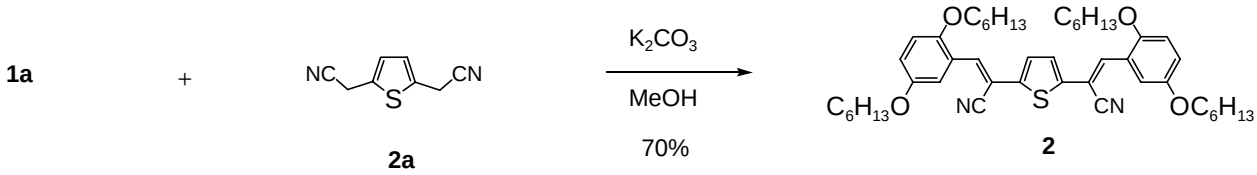
The synthetic routes used to build up oligomers (**1**)-(**6**), which bear mono-, di-, or trithienyl rings at the central position with or without cyano groups on the α-position to the thienyl rings were shown in **Schemes I-IV**. Thus, the preparation of compound (**1**) was carried out in satisfactory yield by using NaH as the base in the Wittig-Emmons reaction from 2,5-dihexyloxybenzaldehyde (**1a**)[17] and tetraethyl thiophene-2,5-diylbismethylphosphonate (**1b**)[18] in DMF at room temperature. NMR spectral data of the crude reaction mixture showed that *trans,trans*-form was obtained as the major product (≥95%). Compound (**2**) in *trans,trans*-form was obtained by Knoevenagel condensation[19] of monoaldehyde (**1a**) with dicyano compound (**2a**).[20] The stereochemistry of the vinylene linkage in **2** was confirmed by 2D NOESY ^{1}H-NMR spectral analysis. Thus, the cross peaks appeared between the vinylene proton (δ 7.85 ppm) and the proton on the thienylene ring (δ 7.32 ppm). The palladium-catalyzed homocoupling reaction of aryl iodides (**3a** and **4a**) to form **3** and **4** in good yields were carried out by synthetic routes recently reported by our laboratory.[21] The compounds (**3a**) and (**4a**) were prepared in reasonable yields as shown in **Scheme V** and **Scheme VI**, respectively. Thus, 2-diethoxyphosphorylmethyl-5-iodothiophene, obtained from the iodination of diethyl thiophen-2-ylmethylphosphonate[22] in 80% yield, reacted with monoaldehyde (**1a**) under basic conditions could give **3a** in 76% yield. Compound (**4a**) could be obtained in similar yields either from the initial iodination of 2-(2-thienyl)ethanenitrile[23] and following the Knoevenagel condensation with monoaldehyde (**1a**) or from the Knoevenagel condensation of monoaldehyde (**1a**) with 2-(2-thienyl)ethanenitrile first and following the iodination of the corresponding condensation product.

Compounds (**5**) and (**6**) were afforded by using Stille cross-coupling reaction[24] of using 2,5-bis(trimethyltin)thiophene[25] and the corresponding aryl iodide (**3a**) or (**4a**) in THF. All the above synthesized oligomers have satisfactory ^{1}H-, ^{13}C-NMR, 2D NOESY ^{1}H-NMR, and MS spectra as well as the HRMS or elementary analysis.

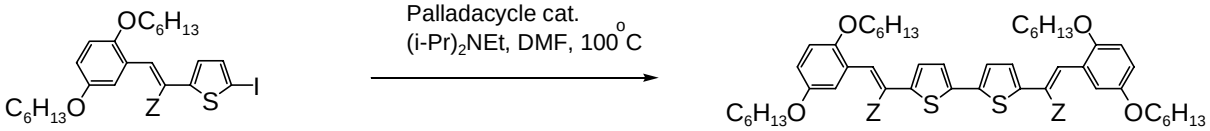
Scheme I. Preparation of Oligomer (**1**) by Wittig-Emmons Reactions.



Scheme II. Preparation of Oligomer (**2**) by Knoevenagel Condensation.



Scheme III. Preparation of Oligomers (**3**) and (**4**) by Pd-Catalyzed Homocoupling Reactions.



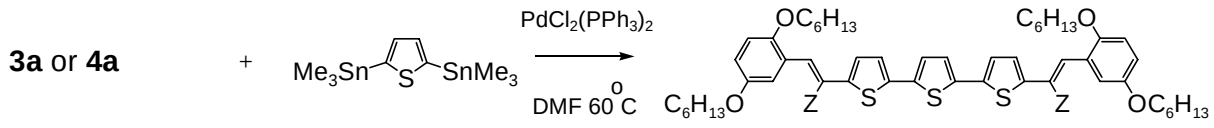
3a Z = H

4a **Z =** CN

3 Z = H 63%

4 Z = CN 42%

Scheme IV. Preparation of Oligomers (**5**) and (**6**) by Stille Cross Coupling Reactions.



5 Z = H 67%

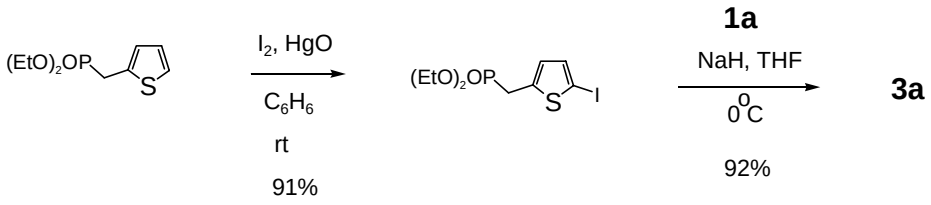
6 Z = CN 55%

The λ_{max} of UV spectra of these oligomers (**1**)-(**6**) showed that thiophene ring indeed could lead to a large red shift due to the overall stabilization of the frontier orbital levels. Thus, compounds (**5**) (λ_{max}

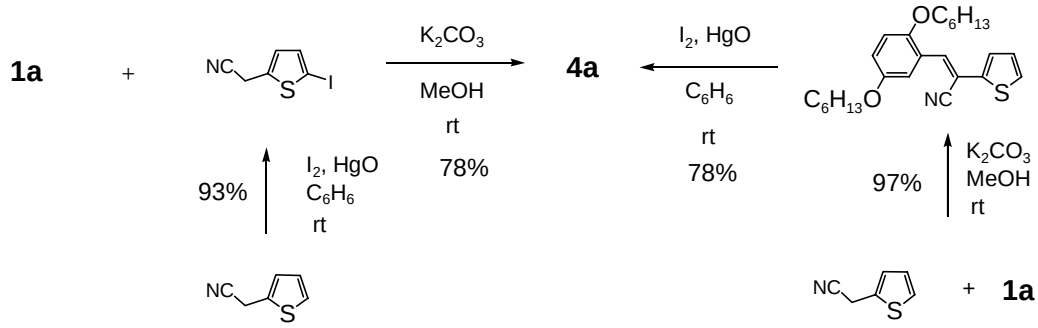
451 nm) and (**6**) (λ_{max} 465 nm) have a slight red shift than compounds (**3**) (λ_{max} 439 nm) and (**4**) (λ_{max} 450 nm) and a bigger red shift than compounds (**1**) (λ_{max} 413 nm) and (**2**) (λ_{max} 431 nm) in their UV spectra. The UV spectral data also showed that the cyano groups in oligomers may induce further red shift than those oligomers without cyano groups.

In conclusion, we have efficiently synthesized some novel alkoxylated phenylene-vinylene-thienylene oligomers with and without cyano substituents at the olefin moieties. Thus, replacement of the central structure of the PPV oligomers with thiophene rings induced a stronger red shift in absorption spectra. Moreover, the cyano groups located on the vinylene moieties α to the central thiophene rings of *p*-phenylene-vinylene-thienylene oligomers gave further red shift than those oligomers without cyano groups.

Scheme V. Preparation of 2-[(1*E*)-2-(5-Iodo(2-thienyl))vinyl]-1,4-dihexyloxybenzene (**3a**).



Scheme VI. Preparation of (2*Z*)-3-(2,5-Dihexyloxyphenyl)-2-[5-iodo(2-thienyl)]prop-2-enenitrile (**4a**).



EXPERIMENTAL

Solvents were dried by appropriate methods wherever needed. All organic extracts were dried over anhydrous magnesium sulfate. TLC was done on aluminum sheets with precoated silica gel 60 F_{254} (40

× 80 mm) from Merck. Purification by column chromatography was carried out with neutral silica gel 60 (70-230 mesh ASTM). HPLC separation was performed at a flow rate of 0.7 mL/min by the use of two Chemco-Pak 10 x 250 column packed with Chemcosorb 5-ODS-H. GLC analyses were performed by a 3.2 x 3.1 column packed with SE-30 (5% on Chemcosorb W). The purity of each compound was judged to be > 95% by ^{1}H-NMR or ^{13}C-NMR spectral analyses. Mps were taken on a MEL-TEMP capillary tube apparatus and are uncorrected. IR spectra were recorded as either Nujol mulls or in the solution form as denoted. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on either a 300 MHz or 400 MHz instrument, using TMS (0 ppm) and $CDCl_3$ (77.0 ppm) as internal standards. HRMS spectra were collected on an Autospec orthogonal acceleration-time of flight mass spectrometer with a resolution of 6000 (5% valley definition), and fitted with a magnet bypass flight tube. MALDI-MS spectra were collected on spectrometer equipped with a nitrogen laser (337nm) and operated in the delayed extraction reflector mode. MS spectra were determined on a Shimadzu QP-1000 spectrometer or Fisons MD800 GC/MS or VG 70-250S spectrometer. UV and fluorescent spectra were recorded in CH_2Cl_2 solution. Bis(triphenylphosphine)palladium dichloride and palladacycle were prepared by published method.[26,27]

2-((1*E*)-2-{5-[(1*E*)-2-(2,5-Dihexyloxyphenyl)vinyl](2-thienyl)}vinyl)-1,4-dihexyloxybenzene (**1**): To the mixture of **1a** (0.45 g, 1.47 mmol) and sodium hydride (60%, 0.06 g, 1.5 mmol) was added the solution of **1b** (0.28 g, 0.73 mmol) in dry THF (5 mL) under nitrogen at 0 ºC. The reaction mixture was stirred at 0 ºC for another 20 h and quenched with water (10 mL) followed by extraction with ethyl acetate (10 mL x 3). The extraction was washed with brine until neutral and dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography (silica gel, hexanes : ethyl acetate = 5 : 0.1) to give the titled compound as solid (0.37 g, 73%) in yellow color: mp 38 - 39 ºC. ^{1}H NMR ($CDCl_3$, TMS) δ 0.92 (t, *J* = 7 Hz, 6 H), 0.93 (t, *J* = 7 Hz, 6 H), 1.3-1.6 (m, 24 H), 1.7-1.9 (m, 8 H), 3.94 (t, *J* = 7 Hz, 4 H), 3.97 (t, *J* = 7 Hz, 4 H), 6.75 (dd, *J* = 8.9, 2.9 Hz, 2 H), 6.81 (d, *J* = 8.9 Hz, 2 H), 6.92 (s, 2 H), 7.06 (d, *J* = 2.9 Hz, 2 H), 7.21 (d, *J* = 16.2 Hz, 2 H), 7.24 (d, *J* = 16.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, TMS) δ 14.05, 22.64, 25.77, 25.90, 29.43, 31.64, 68.69, 69.62, 112.42, 113.98, 114.64, 122.65, 123.56, 126.72, 127.20, 142.63, 151.02, 153.32 ppm. IR ($CHCl_3$) ν 2957, 2932, 2860, 1731, 1603, 1494, 1468 cm^{-1}; MS *m/z* 688 (M^+). HRMS calcd for $C_{44}H_{64}O_4S$ 688.4525, found 688.4522. Anal. Calcd for $C_{44}H_{64}O_4S$: C, 76.70; H, 9.36. Found: C, 76.38; H, 9.73. UV (CH_2Cl_2) λ_{max} 413 nm.

Em (CH_2Cl_2) λ_{max} 496 nm.

(2*E*)-2-{5-[(1*E*)-2-(2,5-Dihexyloxyphenyl)-1-cyanovinyl](2-thienyl)}-3-(2,5-dihexyloxyphenyl)prop-2-enenitrile (**2**): To the solution of **1a** (0.16 g, 0.5 mmol) and **2a** (0.04 g, 0.25 mmol) in MeOH (5 mL) was added K_2CO_3 (0.07g, 0.5 mmol) and the mixture was stirred for 12 h at rt. The reaction mixture was quenched with water (10 mL) and extracted with ethyl acetate (15 mL x 3). The combined organic layer was washed with saturated brine (10 mL x 2), dried, filtered, concentrated, and followed by column chromatography (silica gel, hexanes : ethyl acetate = 5 : 0.1) to give the title compound as solid (0.13 g, 70%) in red color: mp 42 - 43 ºC. ^{1}H NMR ($CDCl_3$, TMS) δ 0.87 (t, *J* = 7 Hz, 6 H), 0.92 (t, *J* = 7 Hz, 6 H), 1.3-1.6 (m, 24 H), 1.7-1.9 (m, 8 H), 3.99 (t, *J* = 7 Hz, 8 H), 6.86 (d, *J* = 9.0 Hz, 2 H), 6.96 (dd, *J* = 9.0, 2.6 Hz, 2 H), 7.32 (s, 2 H), 7.73 (d, *J* = 2.6 Hz, 2 H), 7.85 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, TMS) δ 13.96, 14.01, 22.61, 25.72, 25.78, 29.19, 29.25, 31.53, 31.59, 68.80, 69.45, 104.90, 112.57, 113.57, 116.63, 119.83, 122.90, 127.28, 135.39, 140.22, 152.03, 153.00 ppm. IR ($CHCl_3$) ν 2931, 2860, 2304, 1734, 1606, 1494, 1468, 1420 cm^{-1}; MS *m/z* 738 (M^+). HRMS calcd for $C_{46}H_{62}N_2O_4S$ 738.4430, found 738.4431. Anal. Calcd for $C_{46}H_{62}N_2O_4S$: C, 74.76; H, 8.46; N, 3.79. Found: C, 74.65; H, 8.27; N, 3.50. UV (CH_2Cl_2) λ_{max} 431 nm. Em (CH_2Cl_2) λ_{max} 524 nm.

2-Diethoxyphosphorylmethyl-5-iodothiophene: To the solution of 2-diethoxyphosphoxyl-methylthiophene (1.15 g, 4.9 mmol) in benzene (10 mL) were added mercuric oxide (1.6 g, 7.4 mmol) and iodine (1.8 g, 7.0 mmol) and the mixture was stirred for 15 h at rt. The reaction mixture was diluted with ethyl acetate (10 mL) and washed with saturated sodium thiosulfate solution (10 mL x 2) and saturated brine (10 mL x 2). The combined organic layer was dried, filtered, concentrated at low pressure, and followed by column chromatography (silica gel, CH_2Cl_2 : ethyl acetate = 5 : 1) to give the titled compound as pale yellow oil (1.61 g, 91%): ^{1}H NMR ($CDCl_3$, TMS) δ 1.22 (t, *J* = 7.0 Hz, 6 H), 3.28 (d, *J* = 20.8 Hz, 2 H), 4.06 (quintet, *J* = 7 Hz, 4 H), 6.59 (t, *J* = 3.6 Hz, 1 H), 7.02 (d, *J* = 3.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, TMS) δ 16.28, 16.36, 27.21, 29.12, 62.44, 62.52, 71.74, 71.81, 128.97, 129.09, 136.81, 136.84, 138.58, 138.71 ppm; IR ($CHCl_3$) ν 1605, 1534, 1429, 1393 cm^{-1}; MS *m/z* 360 (M^+ + Na), 332, 222.

2-[(1*E*)-2-(5-Iodo(2-thienyl))vinyl]-1,4-dihexyloxybenzene (**3a**): To the solution of **1a** (1.53 g, 5 mmol)

in THF (5 mL) was sequentially added sodium hydride (60%, 0.2 g, 5 mmol) and the solution of 2-diethoxyphosphorylmethyl-5-iodothiophene (1.8 g, 5 mmol) in THF (5 mL) under nitrogen atmosphere at 0 ºC. The reaction mixture was stirred for 20 h at 0 ºC, then warmed up slowly to the rt. The reaction mixture was poured into water (20 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed to neutral with saturated brine, dried, filtered, concentrated, followed by column chromatography (silica gel, hexanes : ethyl acetate = 5 : 0.1) to give the title compound as pale yellow oil (2.36 g, 92%): ^{1}H NMR ($CDCl_3$, TMS) δ 0.90 (t, *J* = 7 Hz, 3 H), 0.92 (t, *J* = 7 Hz, 3 H), 1.3-1.6 (m, 12 H), 1.7-1.9 (m, 4 H), 3.92 (t, *J* = 7 Hz, 2 H), 3.94 (t, *J* = 7 Hz, 2 H), 6.68 (d, *J* = 3.6 Hz, 1 H), 6.74 (dd, *J* = 8.9, 2.6 Hz, 1 H), 6.80 (d, *J* = 8.9 Hz, 1 H), 7.02 (d, *J* = 2.6 Hz, 1 H), 7.12 (d, *J* = 3.6 Hz, 1 H), 7.16 (d, *J* = 16 Hz, 1 H), 7.17 (d, *J* = 16 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, TMS) δ 14.02, 22.60, 25.73, 25.89, 29.38, 31.60, 68.64, 69.51, 71.87, 112.35, 113.86, 114.88, 121.35, 124.46, 126.62, 126.94, 137.42, 149.80, 151.00, 153.23 ppm; IR ($CHCl_3$) ν 1603, 1577, 1494, 1468, 1428 cm^{-1}; MS *m/z* 512 (M^+), 427, 386, 223. HRMS calcd for $C_{24}H_{33}NO_2IS$ 512.1246, found 512.1248.

(2*Z*)-3-(2,5-Dihexyloxyphenyl)-2-(2-thienyl)prop-2-enenitrile: To the solution of **1a** (3.0 g, 10 mmol) and thiophene-2-acetonitrile (1.23 g, 10 mmol) in MeOH (10 mL) was added K_2CO_3 (1.38 g, 10 mmol) at rt and the mixture was stirred for another 10 h. The reaction mixture was then quenched with water (15 mL) and extracted with ethyl acetate (10 mL x 3). The combined extraction was washed with saturated brine (10mL x 2), dried, filtered, concentrate, and purified by column chromatography (silica gel, hexanes : ethyl acetate = 5 : 0.2) to give the title compound as yellow solid (4.0 g, 97%): mp 42 - 43 ºC. ^{1}H NMR ($CDCl_3$, TMS) δ 0.92 (t, *J* = 7 Hz, 6 H), 1.3-1.6 (m, 12 H), 1.7-1.9 (m, 4 H), 3.9-4.0 (m, 4 H), 6.85 (d, *J* = 8.9 Hz, 1 H), 6.94 (dd, *J* = 8.9, 2.9 Hz, 1 H), 7.06 (dd, *J* = 5.2, 3.8 Hz, 1H), 7.27 (d, *J* = 5.2 Hz, 1 H), 7.36 (d, *J* = 3.8 Hz, 1 H), 7.73 (d, *J* = 2.9 Hz, 1 H), 7.85 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, TMS) δ 13.99, 22.58, 25.71, 25.81, 29.25, 31.53, 31.58, 68.76, 69.41, 105.35, 112.58, 113.53, 117.11, 119.28, 123.11, 125.83, 126.64, 127.94, 134.75, 139.97, 151.88, 152.96 ppm. IR ($CHCl_3$) ν 2217, 1604, 1571, 1492, 1467 cm^{-1}; MS *m/z* 411 (M^+), 328, 244. HRMS calcd for $C_{25}H_{33}NO_2S$ 411.2232, found 411.2224.

(2*Z*)-3-(2,5-Dihexyloxyphenyl)-2-[5-iodo(2-thienyl)]prop-2-enenitrile (**4a**): To the solution of

(2*Z*)-3-(2,5-dihexyloxyphenyl)-2-(2-thienyl)prop-2-enenitrile (0.4 g, 10 mmol) in benzene (1.5 mL) was added mercuric oxide (10.7 g, 50 mmol) and iodine (12.5 g, 50 mmol) and the mixture was stirred at rt for 20 h. Ethyl acetate (20 mL) was added to dilute the reaction mixture and the mixture was sequentially washed with saturated sodium thiosulfate (15 mL x 2) and brine (15 mL x 2). The combined organic layer was dried, filtered, concentrated, and followed by column chromatography (silica gel, hexanes : ethyl acetate = 5 : 0.2) to give the title compound as solid (4.2 g, 78%) in orange yellow color: mp 47 - 48 ºC. ^{1}H NMR ($CDCl_3$, TMS) δ 0.90 (t, *J* = 7 Hz, 3 H), 0.92 (t, *J* = 7 Hz, 3 H), 1.3-1.6 (m, 12 H), 1.7-1.9 (m, 4 H), 3.9-4.0 (m, 4 H), 6.83 (d, *J* = 9.0 Hz, 1 H), 6.93 (dd, *J* = 9.0, 2.7 Hz, 1 H), 7.00 (d, *J* = 3.8 Hz, 1 H), 7.20 (d, *J* = 3.8 Hz, 1 H), 7.71 (d, *J* = 2.7 Hz, 1 H), 7.74 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, TMS) δ 14.02, 22.58, 22.63, 25.72, 25.86, 29.26, 31.58, 68.75, 69.42, 74.05, 104.26, 112.37, 113.54, 116.67, 119.70, 122.78, 127.82, 135.24, 137.83, 145.59, 151.99, 152.95 ppm. MS *m/z* 537 (M^+), 454, 411, 370, 242. HRMS calcd for $C_{25}H_{32}NO_2IS$ 537.1198, found 537.1201.

2-[(1*E*)-2-(5-{5-[(1*E*)-2-(2,5-Dihexyloxyphenyl)vinyl](2-thienyl)}(2-thienyl))vinyl]-1,4-dihexyloxy-benzene (**3**): Under nitrogen atmosphere, **3a** (0.8 g, 1.56 mmol) and palladacycle catalyst (8 mg, 0.008 mmol) in DMF (5 mL) were added to *N*,*N*-diisopropylethylamine (1.0 g, 7.75 mmol) at rt. The reaction mixture was then stirred at 100 ºC for 12 h. The reaction mixture was then cooled to rt, quenched with water (20 mL) and extracted with ethyl acetate (10 mL x 4). The extraction was washed with brine (10 mL x 2), dried, filtered, concentrated, and followed by column chromatography (silica gel, hexanes : CH_2Cl_2 : ethyl acetate = 5 : 1 : 0.01) to give the title compound as solid (0.38 g, 63%) in yellow color: mp 72 - 74 ºC. ^{1}H NMR ($CDCl_3$, TMS) δ 0.92 (t, *J* = 7 Hz, 6 H), 0.94 (t, *J* = 7 Hz, 6 H), 1.3-1.6 (m, 24 H), 1.78 (quintet, *J* = 6.7 Hz, 4 H), 1.84 (quintet, *J* = 6.7 Hz, 4 H), 3.95 (t, J = 6.6 Hz, 4 H), 3.97 (t, *J* = 6.6 Hz, 4 H), 6.75 (dd, *J* = 8.9, 2.9 Hz, 2 H), 6.82 (d, *J* = 8.9 Hz, 2 H), 6.94 (d, *J* = 3.7 Hz, 2 H), 7.06 (d, *J* = 2.9 Hz, 2 H), 7.07 (d, *J* = 3.7 Hz, 2 H), 7.22 (s, 4 H) ppm. ^{13}C NMR ($CDCl_3$, TMS) δ 14.04, 22.60, 22.65, 25.74, 25.93, 29.40, 31.62, 68.67, 69.60, 112.27, 113.96, 114.72, 122.15, 123.58, 123.95, 126.87, 127.01, 136.11, 142.80, 150.97, 153.28 ppm. IR ($CHCl_3$) ν 2932, 2860, 1714, 1603, 1496, 1468 cm^{-1}; MS *m/z* 770 (M^+), 703, 576. HRMS calcd for $C_{48}H_{66}O_4S_2$ 770.4394, found 770.4394. Anal. Calcd for $C_{48}H_{66}O_4S_2$: C, 74.76; H, 8.63. Found: C, 74.80; H, 8.67. UV (CH_2Cl_2) λ_{max} 439 nm. Em (CH_2Cl_2) λ_{max} 507 nm.

2-(5-{5-[(1*E*)-2-(2,5-Dihexyloxyphenyl)-1-cyanovinyl](2-thienyl)}(2-thienyl))(2*Z*)-3-(2,5-dihexyl-oxyphenyl)prop-2-enenitrile (**4**): Followed the similar procedure as described in the preparation of **3** by using **4a** (1.1 g, 2 mmol), palladacycle catalyst (10 mg, 0.01 mmol), *N*,*N*-diisopropylethylamine (1.3 g, 10 mmol) in DMF (8 mL) gave the title compound as solid (0.35g, 42%) in orange red color: mp 127 - 128 ºC. ^{1}H NMR ($CDCl_3$, TMS) δ 0.91 (t, *J* = 7 Hz, 6 H), 0.92 (t, *J* = 7 Hz, 6 H), 1.3-1.6 (m, 24 H), 1.7-1.9 (m, 8 H), 3.99 (t, *J* = 7 Hz, 8 H), 6.86 (d, *J* = 9.0 Hz, 2 H), 6.95 (dd, *J* = 9.0, 2.7 Hz, 2 H), 7.15 (d, *J* = 3.8 Hz, 2 H), 7.29 (d, *J* = 3.8 Hz, 2 H), 7.75 (d, *J* = 2.7 Hz, 2 H), 7.82 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, TMS) δ 14.06, 22.62, 22.70, 25.76, 25.92, 29.30, 31.62, 68.83, 69.49, 104.94, 112.50, 113.60, 116.76, 119.65, 123.04, 124.90, 127.60, 134.59, 136.97, 139.59, 152.03, 153.04 ppm. IR ($CHCl_3$) ν 2987, 2933, 2860, 2304, 1734, 1606, 1493, 1468, 1421 cm^{-1}; MS *m/z* 820 (M^+). HRMS calcd for $C_{50}H_{64}N_2O_4S_2$ 820.4308, found 820.4299. Anal. Calcd for $C_{50}H_{64}N_2O_4S_2$: C, 73.13; H, 7.86; N, 3.41. Found: C, 72.75; H, 7.79; N, 3.18. UV (CH_2Cl_2) λ_{max} 450 nm. Em (CH_2Cl_2) λ_{max} 532 nm.

2-{(1*E*)-2-[5-(5-{5-[(1*E*)-2-(2,5-Dihexyloxyphenyl)vinyl](2-thienyl)}(2-thienyl))(2-thienyl)]vinyl}-1,4-dihexyloxybenzene (**5**): Under nitrogen atmosphere, **3a** (0.42 g, 0.8 mmol), 2,5-bis(trimethylstannyl)thiophene (0.16 g, 0.4 mmol) and $Pd(PPh_3)_2Cl_2$ (5 mg, 0.07 mmd) in DMF (5 mL) were stirred at 60°C for 24 h and worked up in the similar way as described in **3** to give the title compound as solid (0.22 g, 67%) in orange red color: mp 84 - 85 ºC. ^{1}H NMR ($CDCl_3$, TMS) δ 0.92 (t, *J* = 7 Hz, 6 H), 0.95 (t, *J* = 7 Hz, 6 H), 1.3-1.6 (m, 24 H), 1.7-1.9 (m, 8 H), 3.95 (t, *J* = 7 Hz, 4 H), 3.98 (t, *J* = 7 Hz, 4 H), 6.76 (dd, *J* = 8.9, 2.9 Hz, 2 H), 6.81 (d, *J* = 8.9 Hz, 2 H), 6.94 (d, *J* = 3.8 Hz, 2 H), 7.06 (d, *J* = 2.9 Hz, 2 H), 7.07 (d, *J* = 3.8 Hz, 2 H), 7.09 (s, 2 H), 7.21 (d, *J* = 16.6 Hz, 2 H), 7.23 (d, *J* = 16.6 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, TMS) δ 14.09, 22.64, 22.70, 25.78, 25.98, 29.47, 31.67, 68.69, 69.62, 112.31, 113.99, 114.77, 122.09, 123.74, 124.05, 124.27, 126.89, 126.99, 135.60, 136.41, 143.01, 151.02, 153.33 ppm. IR ($CHCl_3$) ν 2932, 2859, 1712, 1605, 1494 cm^{-1}; MS *m/z* 852 (M^+), 770. HRMS calcd for $C_{52}H_{68}O_4S_3$ 852.4280, found 852.4293. Anal. Calcd for $C_{52}H_{68}O_4S_3$: C, 73.19; H, 8.03. Found: C, 72.79; H, 7.80. UV (CH_2Cl_2) λ_{max} 451 nm. Em (CH_2Cl_2) λ_{max} 526 nm.

2-[5-(5-{5-[(1*E*)-2-(2,5-Dihexyloxyphenyl)-1-cyanovinyl](2-thienyl)}(2-thienyl))(2-thienyl)](2Z)-3-(2,5-dihexyloxyphenyl)prop-2-enenitrile (**6**): Followed the similar procedure as described in the preparation of **5** by using **4a** (0.9 g, 1.67 mmol), 2,5-bis(trimethylstannyl)thiophene (0.34 g, 0.83

mmol), and $Pd(PPh_3)_2Cl_2$ (10 mg, 0.174 mmol) in DMF (10 mL) gave the title compound as solid (0.41g, 55%) in red color: mp 154 - 155 ºC. ^{1}H NMR ($CDCl_3$, TMS) δ 0.91 (t, *J* = 7 Hz, 6 H), 0.93 (t, *J* = 7 Hz, 6 H), 1.3-1.6 (m, 24 H), 1.7-1.9 (m, 8 H), 3.99 (t, *J* = 7 Hz, 8 H), 6.85 (d, *J* = 9.0 Hz, 2 H), 6.94 (dd, *J* = 9.0, 2.8 Hz, 2 H), 7.13 (s, 2 H), 7.14 (d, *J* = 3.9 Hz, 2 H), 7.28 (d, *J* = 3.9 Hz, 2 H), 7.75 (d, *J* = 2.8 Hz, 2 H), 7.81 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, TMS) δ 14.03, 14.08, 22.61, 22.71, 25.75, 25.96, 29.32, 31.63, 68.82, 69.50, 104.98, 112.46, 113.61, 116.79, 119.57, 123.10, 124.46, 125.07, 127.63, 134.31, 136.24, 137.22, 139.17, 151.99, 153.04 ppm. IR ($CHCl_3$) ν 2986, 2932, 2861, 2305, 1734, 1606, 1420 cm^{-1}; MS *m/z* 902 (M^+). HRMS calcd for $C_{54}H_{66}N_2O_4S_3$ 902.4185, found 902.4181. Anal. Calcd for $C_{54}H_{66}N_2O_4S_3$: C, 71.80; H, 7.36; N, 3.10. Found: C, 71.89; H, 7.40; N, 2.98. UV (CH_2Cl_2) λ_{max} 465 nm. Em (CH_2Cl_2) λ_{max} 553 nm.

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