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Synthesis of oligo(*p*-phenylene–vinylene–thienylene)s as potential red light-emitting materials

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Abstract—Several potential red light-emitting oligomers containing alkoxylated phenylene–vinylene–thienylene backbones with and without cyano groups at the olefin moieties have been designed and synthesized. The influences of the skeleton as well as the position of the cyano groups in the vinylene moiety to the absorption and emission spectra of these new oligomers are also discussed.

1. Introduction

The synthesis of new oligo(phenylene–vinylene) (OPV) derivatives has attracted considerable attention[1] because of their widespread application in light-emitting diodes,[2] chemical sensors,[3] nonlinear optics,[4] organic magnetic materials,[5] and flat-panel displays.[6] For full-color applications, it is necessary to have a set of red, green, and blue emitters with sufficiently high luminous efficiency and proper chromaticity. After one decade of intensive research, organic materials for green and blue organic light-emitting diodes (OLED) with high luminance, high efficiency, saturated emission, and practical lifetimes have been developed.[7] However, to date, the corresponding development of organic materials for red electroluminescence lags significantly behind that for the other two primary colors. Presently, most high-performance red OLED are made by doping a red dye into a suitable host.[8] However, their performance as red emitters is still significantly inferior to that of the prototypical green and blue emitters. This problem of color purity is partly due to the fact that a significant portion of the photoluminescence (PL) peaks of their emission spectra of these compounds are below 600 nm, and thus they cannot emit a saturated red color. Thus, the emission peaks of the dopants have to be shifted further to the long wavelength region, so that the emission below 600 nm can be substantially reduced. Therefore, there still remains much room for improvement on the materials for red OLED. Our preliminary results from ZINDO calculations[9] on our previous PPV type oligomers[10] and with thiophene ring to replace the phenylene moieties showed that thiophene ring could cause large red shifts in the absorption spectra.[11] The presence of the alkoxy unit should enhance the solubility of oligomers and the introduction of high electron affinity of cyano groups on the vinylene linkages of OPV derivatives has been reported to lower the energy of the LUMO and reduces the barrier to the electron injection in LED.[12] 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.[13] However, despite its interesting properties in this field, as to our knowledge, there is no report in the literature about the synthesis of the oligo(phenylene–vinylene-thiophene)s (OPVTs) containing with or without cyano groups on the vinylene linkage.[14] Herein, we report the design and synthesis of a new family of functionalized OPVTs **1**–**4** (Fig. 1) with definable skeletons that containing a cyano group at the various position of the vinylene moiety to strengthen the efficiency of the electron delocalization within conjugation skeletons.[15] This design was aimed at producing an efficient red OPVT dye.

2. Results and discussion

Scheme 1 shows the synthetic protocols for the four target molecules **1**–**4**. Thus, the Horner–Wadsworth–Emmons reaction of 2,5-bishexyloxybenzenedicarbaldehyde **5**[16] and 2-(diethoxyphosphorylmethyl)thiophene[17] could give mono condensation product **6** along with some condensation product at both ends (~25% yield). After column chromatography, compound **6** was isolated in 39% yield. The Horner–Wadsworth–Emmons reaction of 2,5-bis-(diethoxyphosphorylmethyl)thiophene[18] with 2 equiv. of

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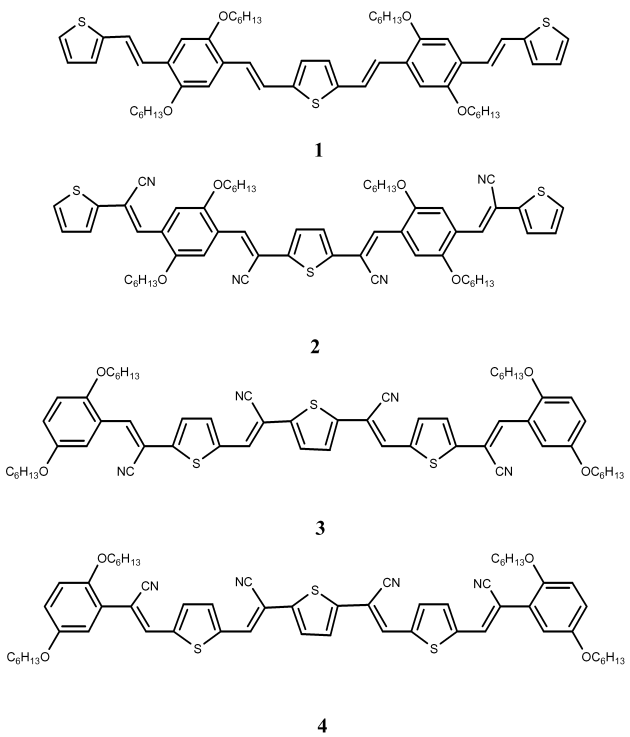
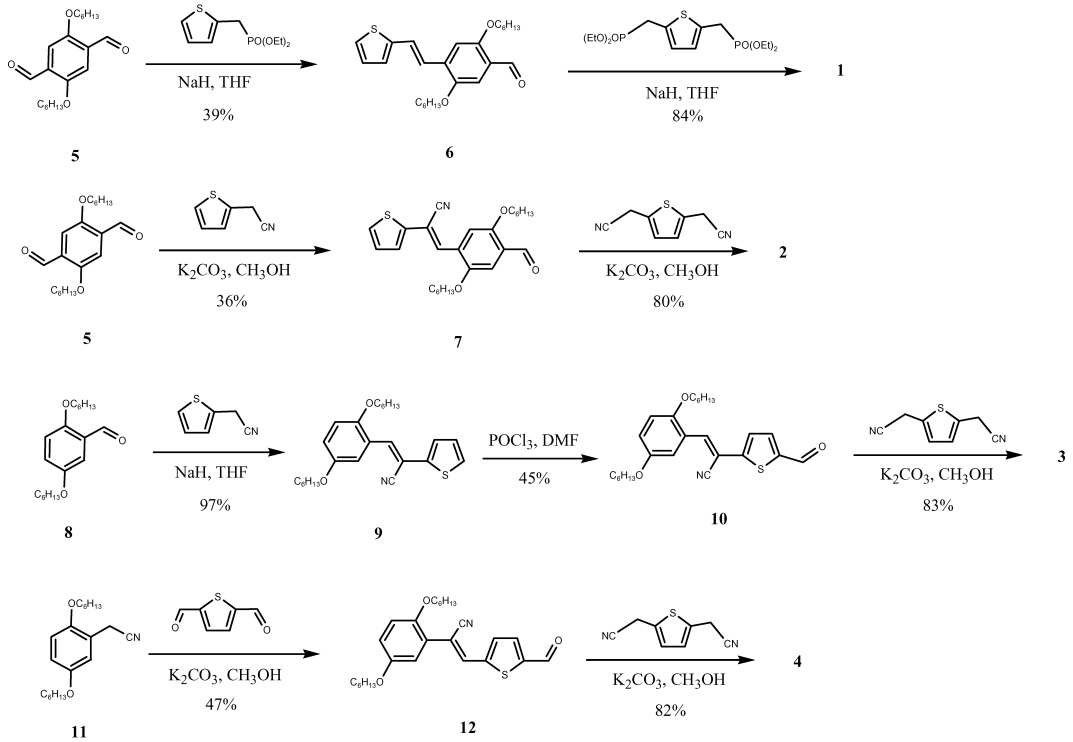


Figure 1. Alkoxylated phenylene–vinylene–thienylene oligomers **1**–**4**.

compound **6** could give compound **1** in 84% isolated yield. The stereochemistry of the vinylene linkages were confirmed by ^{1}H NMR spectral analysis. Similarly, the Knoevenagel condensation of thiophene-2-acetonitrile[19] and dialdehyde **5** could give mono-aldehyde **7** in 36% yield. The following another Knoevenagel reaction of 2,5-bis(cyanomethyl)thiophene[20] with 2 equiv. of compound **7** could give compound **2** in 80% isolated yield. The *E*-form stereochemistry of the vinylene moieties in compound **2** were determined by its 2D NOESY ^{1}H NMR spectral analysis. The condensation of 2,5-dihexyloxybenzaldehyde **8**[21] with thiophene-2-acetonitrile can afford compound **9** in 97% yield. Formylation of compound **9** via Vilsmeier–Haack reaction by using phosphorus oxychloride and *N*,*N*-dimethylformamide gave mono-aldehyde **10** regioselectively at α-position of the thienyl group. Knoevenagel reaction of 2 equiv. of compound **10** with 1 equiv. of 2,5-bis(cyanomethyl)thiophene could afford compound **3** in 83% yield. Knoevenagel condensation of 2,5-thiophenedicarboxaldehyde with 2,5-dihexyloxybenzacetonitrile **11**[22] could give mono-aldehyde **12** in 47% yield. Another Knoevenagel condensation of 2 equiv. of compound **12** with 2,5-bis(cyanomethyl)thiophene could afford compound **4** in 82% isolated yield.

Figure 2 shows the UV and PL spectra of oligomers **1**–**4** and the λ_{max} of their UV and PL spectral data are shown in Table 1. Molecules with these definable conjugation skeletons show that the PL peaks of their emission spectra of these compounds may reach to pure red emission in solutions. The λ_{max} of UV spectra for **1**–**4** are 469, 510, 514, 514 nm, respectively. While the λ_{max} of PL spectra for **1**–**4** are 567, 602, 644, 615 nm, respectively. The fluorescence quantum yields for **1**–**4** in chloroform solution are 0.11, 0.26, 0.05, 0.15, respectively. Interestingly, compound **1** with no cyano groups on the vinylene moiety gave lowest λ_{max} in both UV and PL spectra. The addition of cyano groups on the OPVT skeletons results in red shifts in both UV and PL spectra. The red shifts range from 41 to 45 nm in UV absorption while 35–77 nm in PL emission. It is interesting to know that the position of the cyano groups on the vinylene moieties gave only small differences (0–4 nm) in UV absorption spectra of **2**–**4**. However, it could cause a



Scheme 1. Synthetic procedures for oligomers **1**–**4**.

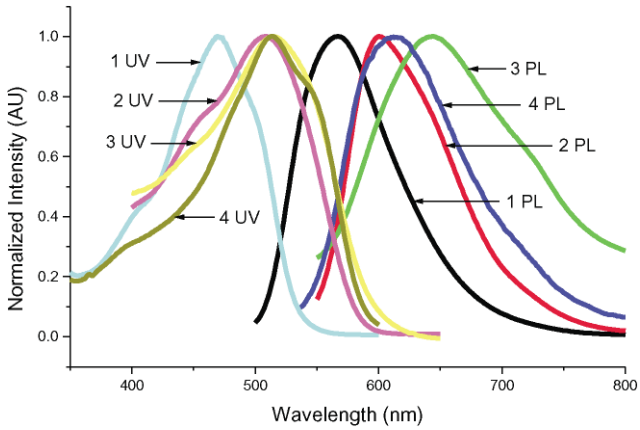


Figure 2. The UV and PL spectra (in CH_2Cl_2) of oligomers **1**–**4**.

Table 1. The λ_{max} of UV and PL in CH_2Cl_2 and Φ_F in $CHCl_3$ for oligomers **1**–**4**

Compound	UV λ_{max} (nm)	PL λ_{max} (nm)	Φ_F[a]
1	469	567	0.11
2	510	602	0.26
3	514	644	0.05
4	514	615	0.15

[a] Use Nile Red ($\Phi_F \cong$ 0.33) to compare with in $CHCl_3$.[23]

big difference (13–42 nm) in PL emission in **2**–**4**. Compound **2** with only one vinylene-thienylene-vinylene moiety in the middle skeleton and with four cyano groups attached at α-position of the vinylene moieties gave a small blue shift in both UV and PL spectra (4 and 13 nm, respectively) than that of compound **4**, but, gave a big blue shift in PL spectra (42 nm) than that of compound **3**. Compound **3** with three thienylene-vinylene linkages in the middle of the skeleton and with four cyano groups attached at α-position of the vinylene moieties for the 2-thienyl units gave the highest λ_{max} in both UV and PL spectra. Compound **4** with only two cyano groups attached at α-position of the vinylene moieties for the 2-thienyl units gave significant blue shift (~29 nm) than that of compound **3**. Thus, the more thienylene-vinylene linkages and the more cyano groups attached at α-position of the vinylene moieties for the 2-thienyl units gave significant red shifts in PL spectra. The preparation of devices and their electro-optical properties are still under active investigation in our collaborator's lab, and their results will be reported elsewhere when they are available.

3. Conclusion

Four alkoxylated phenylene–vinylene–thienylene oligomers have been synthesized efficiently. The emission wavelength of oligomers **3** and **4** have reached to the range of red light-emitting. Our results show that the more thienylene-vinylene linkages and the more cyano groups attached at α-position of the vinylene moieties for the 2-thienyl units gave significant red shifts in both absorption and emission spectra. The relationship between the position of thiophene and cycno group and their absorption and emission spectra of these oligomers is very interesting as compared to the phenylene analogues and need to have further studied.

4. Experimental

4.1. General procedure

THF was 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). 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 were 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 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 (337 nm) 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.

4.1.1. Preparation of 4-[(1*E*)-2-(2-thienyl)vinyl]-2,5-dihexyloxybenzaldehyde 6. To a solution of compound **5**[16] (0.33 g, 1.0 mmol) and NaH (0.024 g, 1.0 mmol) in dry THF (5 mL) was added dropwise the solution of 2-(diethoxyphosphorylmethyl)thiophene[17] (0.23 g, 1.0 mmol) in dry THF (5 mL), the mixture was stirred at 0°C for 4 h. then poured into water (20 mL), extracted with EtOAc (10 mL×3). Organic layer was washed with brine (3×50 mL), dried over $MgSO_4$. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane/EtOAc=25:1) to give compound **6** as a yellow solid (0.16 g, 39%). Mp 52–53°C. IR (CH_2Cl_2) 3050, 2933, 2930, 2872, 2859, 1675, 1598, 1487, 1468, 1423, 1387 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, *J*=7 Hz, 6H), 1.35–1.38 (m, 8H), 1.50–1.53 (m, 4H), 1.82–1.87 (m, 4H), 4.03 (t, *J*=6.4 Hz, 2H), 4.11 (t, *J*=6.4 Hz, 2H), 7.03 (dd, *J*=3.0, 5.0 Hz, 1H), 7.10 (s, 1H), 7.13 (d, *J*=3.0 Hz, 1H), 7.25 (d, *J*=16.0 Hz, 1H), 7.26 (d, *J*=5.0 Hz, 1H), 7.31 (s, 1H), 7.43 (d, *J*=16.0 Hz, 1H), 10.44 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.03, 22.61, 25.76, 25.84, 29.18, 31.54, 69.10, 69.18, 110.09, 110.57, 122.66, 124.04, 125.38, 125.50, 127.00, 127.74, 133.85, 143.01, 150.67, 156.17, 189.13 ppm. MS *m*/*z* 414 (M^+), HRMS calcd for $C_{25}H_{34}O_3S$ 414.2229, found 414.2237.

4.1.2. Preparation of 1-[(1*E*)-2-(5-{(1*E*)-2-[4-((1*E*)-2-(2-thienyl)vinyl)-2,5-di- hexyloxphenyl]vinyl}(2-thienyl))-vinyl]-4-((1*E*)-2-(2-thienyl)vinyl)-2,5-dihexyloxy-benzene 1. Compound **6** (0.21 g, 0.5 mmol) and 2,5-bis(diethoxyphosphorylmethyl)-thiophene[18] (0.1 g, 0.25 mmol) were dissolved in dry THF (5 mL), and NaH (0.012 g, 0.5 mmol) was added. The reaction mixture was

stirred at 0°C for 16 h, and then poured into water (20 mL), extracted with EtOAc (10 mL×3), washed with brine (3×50 mL), dried over $MgSO_4$. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2/EtOAc=5:1:0.01) to give oligomer **1** as a red solid (0.19 g, 84%). Mp 99–100°C. IR (CH_2Cl_2) 3056, 2957, 2931, 2858, 1605, 1522, 1494, 1468, 1430, 1419, 1389 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, J=7 Hz, 12H), 1.38–1.42 (m, 16H), 1.54–1.58 (m, 8H), 1.82–1.89 (m, 8H), 3.98–4.04 (m, 8H), 6.93 (s, 2H), 7.01 (d, J=16.0 Hz, 4H), 7.02 (s, 4H), 7.04 (d, J=3.0 Hz, 2H), 7.16 (d, J=5.0 Hz, 2H), 7.23 (dd, J=3.0, 5.0 Hz, 2H), 7.25 (d, J=16.0 Hz, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.06, 22.65, 25.93, 29.43, 31.64, 69.31, 69.47, 110.60, 110.68, 122.07, 122.37, 123.40, 123.45, 124.10, 125.61, 126.35, 126.40, 126.81, 127.53, 142.80, 143.85, 151.04, 151.09 ppm. MS *m/z* 904 (M^+), HRMS calcd for $C_{56}H_{72}O_4S_3$ 904.4593, found 904.4606.

4.1.3. Preparation of (2*E*)-3-(4-formyl-2,5-dihexyloxyphenyl)-2-(2-thienyl)prop-2- enenitrile 7. K_2CO_3 (0.69 g, 5.0 mmol) was added to the solution of compound **5** (1.7 g, 5.0 mmol) and thiophene-2-acetonitrile[19] (0.62 g, 5.0 mmol) in CH_3OH (10 mL). The mixture was stirred at room temperature. After 8 h, the reaction mixture was poured into water (30 mL), extracted with EtOAc (10 mL×3). The organic layer was washed with brine (3×20 mL), dried over $MgSO_4$. The solvent was removed, the residue was purified by column chromatography (silica gel, hexane/EtOAc=5:0.2) to give title compound **7** as a yellow solid (0.8 g, 36%). Mp 41–42°C. IR (CH_2Cl_2) 3054, 2956, 2933, 2872, 2860, 2217, 1680, 1611, 1487, 1467, 1424, 1387 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J=7 Hz, 6H), 1.35–1.37 (m, 8H), 1.57–1.60 (m, 4H), 1.85–1.89 (m, 4H), 4.04 (t, J=6.3 Hz, 2H), 4.15 (t, J=6.3 Hz, 2H), 7.08 (dd, J=3.0, 5.0 Hz, 1H), 7.34 (s, 1H), 7.35 (d, J=5.0 Hz, 1H), 7.42 (d, J=3.0 Hz, 1H), 7.84 (s, 2H), 10.48 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.97, 22.56, 25.74, 29.07, 31.49, 69.25, 69.36, 108.06, 109.85, 112.44, 116.78, 126.25, 126.95, 127.77, 128.19, 129.37, 133.17, 139.39, 151.39, 155.54, 189.07 ppm. MS *m/z* 439 (M^+), HRMS calcd for $C_{26}H_{33}NO_3S$ 439.2181, found 439.2185.

4.1.4. Preparation of (2*E*)-3-{4-[(1*E*)-2-(5-{(1*E*)-2-[4-((1*E*)-2-cyano-2-(2-thienyl)-vinyl)-2,5-dihexyloxyphenyl]-1-cyanovinyl}(2-thienyl))-2-cyanovinyl]-2,5-dihexyloxyphenyl}-2-(2-thienyl)prop-2-enenitrile 2. Compound **7** (0.34 g, 0.78 mmol) and 2,5-bis-(cyanomethyl)thiophene[20] (0.06 g, 0.39 mmol) were dissolved in CH_3OH (5 mL), and K_2CO_3 (0.11 g, 0.8 mmol) was added. The reaction mixture was stirred at room temperature for 16 h, the then poured into water (15 mL), extracted with CH_2Cl_2 (10 mL×3). The organic layer was washed with brine (3×20 mL), dried over $MgSO_4$. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2/EtOAc=5:1:0.01) to give oligomer **2** as a brown solid (0.31 g, 80%). Mp 177–178°C. IR (CH_2Cl_2) 3054, 2984, 2932, 2859, 2218, 1606, 1493, 1468, 1429, 1378 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J=7.0 Hz, 6H), 0.92 (t, J=7.0 Hz, 6H), 1.35–1.56 (m, 24H), 1.84–1.91 (m, 8H), 4.11 (t, J=7.0 Hz, 4H), 4.13 (t, J=7.0 Hz, 4H), 7.08 (dd, J=5.0, 3.4 Hz, 2H), 7.33 (d, J=5.0 Hz, 2H), 7.36 (s, 2H), 7.40 (d, J=3.4 Hz, 2H), 7.84 (s, 2H), 7.85 (s, 2H), 7.88 (s, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.00, 22.62, 25.79, 25.85, 29.07, 29.14, 31.54, 69.45, 69.48, 105.39, 106.38, 110.87, 110.98, 116.67, 117.15, 125.08, 126.05, 126.60, 127.33, 127.88, 128.16, 133.11, 134.05, 139.82, 140.64, 151.50, 151.69 ppm. MS *m/z* 1027 (M^++Na), 1004 (M^+), HRMS calcd for $C_{60}H_{68}N_4O_4S_3$ 1004.4403, found 1004.4416.

4.1.5. Preparation of (2*E*)-3-(2,5-dihexyloxyphenyl)-2-(2-thienyl)prop-2-enenitrile 9. K_2CO_3 (1.38 g, 10 mmol) was added to the solution of 2,5-dihexyloxybenzaldehyde **8**[21] (3.0 g, 10 mmol) and thiophene-2-acetonitrile (1.23 g, 10 mmol) in CH_3OH (10 mL). The mixture was stirred at room temperature for 10 h, and then poured into water (30 mL), extracted with EtOAc (10 mL×3). The organic layer was washed with brine (3×20 mL), dried over $MgSO_4$. The solvent was removed, the residue was purified by column chromatography (silica gel, hexane/EtOAc=5:0.2) to give compound **9** as a yellow solid (4.0 g, 97%). Mp 42–43°C. IR (CH_2Cl_2) 3036, 2951, 2934, 2866, 2859, 2218, 1607, 1575, 1519, 1492, 1467, 1433, 1379, 1340 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J=7 Hz, 6H), 1.30–1.60 (m, 12H), 1.70–1.90 (m, 4H), 3.90–4.01 (m, 4H), 6.85 (d, J=8.9 Hz, 1H), 6.94 (dd, J=8.9, 2.9 Hz, 1H), 7.05 (dd, J=5.2, 3.8 Hz, 1H), 7.27 (d, J=5.2 Hz, 1H), 7.36 (d, J=3.8 Hz, 1H), 7.73 (d, J=2.9 Hz, 1H), 7.85 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 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. MS *m/z* 411 (M^+), HRMS calcd for $C_{25}H_{33}NO_2S$ 411.2232, found 411.2224.

4.1.6. Preparation of (2*E*)-3-(2,5-dihexyloxyphenyl)-2-(5-formyl(2-thienyl))prop-2-enenitrile 10. The mixture of $POCl_3$ (1.61 g, 10.5 mmol) and DMF (0.77 g, 10.5 mmol) was stirred at room temperature for 1 h, and then compound **9** (1.0 g, 2.4 mmol) was added. The reaction mixture was continually stirred at room temperature for 1 h and 60°C for 4 h. After cooling, the mixture was poured into 15% $NaHCO_3$ (20 mL), extracted with EtOAc (10 mL×3). The organic layer was washed with brine (3×20 mL), dried over $MgSO_4$. The solvent was removed, the residue was purified by column chromatography (silica gel, hexane/EtOAc=5:0.2) to give compound **10** as a yellow solid (0.47 g, 45%). Mp 35–36°C. IR (CH_2Cl_2) 2952, 2932, 2873, 2859, 2218, 1673, 1607, 1586, 1494, 1468, 1431, 1387 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J=7 Hz, 6H), 1.36–1.39 (m, 8H), 1.47–1.51 (m, 4H), 1.82–1.87 (m, 4H), 3.99 (m, 4H), 6.86 (d, J=9.0 Hz, 1H), 7.01 (dd, J=2.7, 9.0 Hz, 1H), 7.44 (d, J=4.0 Hz, 1H), 7.72 (d, J=4.0 Hz, 1H), 7.78 (d, J=2.7 Hz, 1H), 8.09 (s, 1H), 9.89 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.98, 22.55, 25.67, 25.74, 29.12, 29.15, 31.46, 31.53, 68.70, 69.33, 104.08, 112.25, 113.45, 120.27, 120.84, 127.00, 135.37, 136.86, 138.08, 142.73, 148.99, 152.43, 152.84, 182.49 ppm. MS *m/z* 439 (M^+), HRMS calcd for $C_{26}H_{33}NO_3S$ 439.2181, found 439.2182.

4.1.7. Preparation of (2*E*)-2-[5-((1*E*)-2-{5-[(1*E*)-2-(2,5-dihexyloxyphenyl)-1-cyano-vinyl](2-thienyl)}-1-cyano-vinyl)(2-thienyl)]-3-{5-[(1*E*)-2-(2,5-dihexyloxyphenyl)-1-cyanovinyl](2-thienyl)}prop-2-enenitrile 3. K_2CO_3

(0.05 g, 0.36 mmol) was added to the solution of compound **10** (0.16 g, 0.36 mmol) and 2,5-bis(cyanomethyl)thiophene (0.03 g, 0.18 mmol) in CH_3OH (5 mL). The mixture was stirred at room temperature for 12 h, and then poured into water (10 mL), extracted with CH_2Cl_2 (10 mL×3). The organic layer was washed with brine (3×15 mL), dried over $MgSO_4$. The solvent was removed, the residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2/EtOAc=5:1:0.02) to give oligomer **3** as a brown solid (0.15 g, 83%). Mp 116–117°C. IR (CH_2Cl_2) 3059, 2953, 2932, 2859, 2215, 1606, 1492, 1467, 1428, 1377 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J=7 Hz, 12H), 1.34–1.37 (m, 16H), 1.48–1.52 (m, 8H), 1.71–1.87 (m, 8H), 3.96–4.02 (m, 8H), 6.86 (d, J=9.0 Hz, 2H), 6.97 (dd, J=9.0, 2.7 Hz, 2H), 7.30 (s, 2H), 7.36 (s, 2H), 7.38 (d, J=4.0 Hz, 2H), 7.53 (d, J=4.0 Hz, 2H), 7.74 (d, J=2.7 Hz, 2H), 7.97 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.02, 14.18, 22.60, 25.77, 29.26, 31.48, 31.60, 68.81, 69.45, 102.99, 104.43, 112.45, 113.56, 116.05, 116.51, 120.46, 122.63, 127.24, 128.10, 131.54, 133.83, 136.87, 137.36, 139.39, 144.97, 152.38, 152.97 ppm. MS m/z 1005 (M^++1), HRMS calcd for $C_{60}H_{68}N_4O_4S_3$ 1005.4481 (M^++1), found 1005.4477.

4.1.8. Preparation of (2*Z*)-2-(2,5-dihexyloxyphenyl)-3-(5-formyl(2-thienyl))prop-2-enenitrile 12. To a solution of 2,5-thiophenedicarboxaldehyde (0.09 g, 0.63 mmol) and K_2CO_3 (0.09 g, 0.63 mmol) in CH_3OH (5 mL) was added dropwise the solution of 2,5-bis(hexyloxyphenyl)acetonitrile **11**[22] (0.20 g, 0.63 mmol) in CH_3OH (2 mL). The mixture was stirred at room temperature for 16 h, and then poured into water (20 mL), extracted with EtOAc (10 mL×3). Organic layer was washed with brine (3×50 mL), dried over $MgSO_4$. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane/EtOAc=25:1) to give compound **12** as a yellow solid (0.13 g, 47%). Mp 96–97°C. IR (CH_2Cl_2) 3050, 2953, 2932, 2870, 2857, 2214, 1673, 1605, 1498, 1468, 1438, 1386 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J=7 Hz, 6H), 1.35–1.38 (m, 8H), 1.46–1.49 (m, 4H), 1.84–1.89 (m, 4H), 3.94 (t, J=6.4 Hz, 2H), 4.01 (t, J=6.4 Hz, 2H), 6.89 (s, 2H), 7.06 (s, 1H), 7.77 (d, J=4.0 Hz, 1H), 7.79 (d, J=4.0 Hz, 1H), 7.87 (s, 1H), 9.96 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.95, 22.53, 25.65, 25.86, 29.16, 29.23, 31.50, 68.75, 69.52, 110.53, 113.89, 115.90, 116.75, 117.57, 123.18, 130.98, 135.72, 136.35, 144.81, 146.16, 150.84, 153.17, 182.70 ppm. MS m/z 439 (M^+), HRMS calcd for $C_{26}H_{33}NO_3S$ 439.2181, found 439.2180.

4.1.9. Preparation of 3-(5-{(1*E*)-2-[5-((1*E*)-2-{5-[(1*Z*)-2-(2,5-dihexyloxyphenyl)-2-cyanovinyl](2-thienyl)}-1-cyanovinyl)(2-thienyl)]-2-cyanovinyl}(2-thienyl))(2*Z*)-2-(2,5-dihexyloxyphenyl)prop-2-enenitrile 4. K_2CO_3 (0.05 g, 0.36 mmol) was added to the solution of compound **12** (0.15 g, 0.34 mmol) and 2,5-bis(cyanomethyl)thiophene (0.03 g, 0.17 mmol) in CH_3OH (5 mL). The mixture was stirred at room temperature for 15 h, and then poured into water (10 mL), extracted with CH_2Cl_2 (10 mL×3). The organic layer was washed with brine (3×15 mL), dried over $MgSO_4$. The solvent was removed, the residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2/EtOAc=5:1:0.02) to give oligomer **4** as a brown solid (0.14 g, 82%). Mp 115–116°C. IR (CH_2Cl_2) 3050, 2959, 2932, 2859, 2213, 1606, 1582, 1499, 1468, 1387 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J=7 Hz, 12H), 1.34–1.36 (m, 16H), 1.42–1.49 (m, 8H), 1.72–1.89 (m, 8H), 3.94 (t, J=6.0 Hz, 4H), 4.02 (t, J=6.0 Hz, 4H), 6.88 (s, 4H), 7.05 (s, 2H), 7.34 (s, 2H), 7.42 (s, 2H), 7.77 (s, 4H), 7.84 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.01, 22.59, 25.71, 25.93, 29.24, 29.30, 31.58, 68.82, 69.64, 104.04, 108.63, 114.00, 115.74, 116.10, 116.62, 118.15, 123.63, 128.47, 131.24, 131.75, 132.35, 136.32, 139.59, 139.96, 142.43, 150.85, 153.25 ppm. MS m/z 1004 (M^+), HRMS calcd for $C_{60}H_{68}N_4O_4S_3$ 1004.4403, found 1004.4417.

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