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Rapid syntheses of oligo(*p*-phenyleneethynylene)s via iterative convergent approach

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Abstract—A general and controlled bidirectional growth strategy enable a very rapid and efficient construction of oligo(phenyleneethynylene)s possessing functional groups such as methylthio and thioacetate groups at both ends. The strategy employs only one reaction type with good to moderate yields to grow the conjugated chains. The synthesis is efficient and can give 23 benzene rings and 22 carbon–carbon triple bonds in the conjugated chains. The compounds are fully characterized by ^{1}H and ^{13}C NMR and UV/vis and fluorescence spectroscopy.

1. Introduction

Recently, conjugated oligomers of precise length have drawn much attention due to their interesting optical, electrical, optoelectronic properties, and their applications in optoelectronic devices such as molecular wires, molecular-scale electronic devices, solar cells, light-emitting diodes, and field-effect transistors.[1–13] Furthermore, since the oligomers of the repeating unit of a polymer are often useful in understanding the properties of a polymer system, this is due to the close analogy of their physical properties, as well as the ease of characterization of the oligomeric system. These compounds can be served as models for analogous polymers and they can also be used for the construction of nanoarchitectures such as molecular wires in molecular scale electronic devices.[1] The precise length and well-defined conjugated oligomers can play an important role because their precise chemical structure and conjugation length may lead to define functionality and facilitate control over their supramolecular structures in the preparation of organic thin films.[14] As to our knowledge, Tour and his co-workers have reported the synthesis of the longest OPE containing 16 benzene rings and 16 carbon–carbon triple bonds so far.[15] Recently, we have reported a very rapid and efficient construction of oligo(*p*-phenylenevinylene)s (OPV) compounds with precise length and possessing functional groups such as aldehyde and mercapto groups at both ends.[16] That strategy employed only one reaction type with high yields and stereoselectivities to grow the conjugated chains. In this paper, we report the similar rapid synthesis of oligo(*p*-phenyleneethynylene)s (OPE) derivatives with thiomethyl (SMe) or thioacetyl (SAc) end groups from the repeating one building block molecule with three benzene rings and four carbon–carbon triple bonds and a series of Sonogashira and desilylation reactions to build one OPE with 23 benzene rings and 22 triple bonds in its conjugation system. Similar oligomer with 23 aromatic rings and 22 carbon–carbon triple bonds in its conjugation system has been reported by Tour and his co-worker.[17]

2. Results and discussion

Our strategy in synthesizing the OPEs was shown in Scheme 1. The key to the overall strategy is the synthesis of building block molecule **1** with three benzene rings and three carbon–carbon triple bonds. In order to control the growth of the OPE chain, it is necessary to effectively block one terminus of the growing OPE chain which was successfully accomplished with monomer **1**. Thus, monomer **1** possesses an iodo group at one end and a trimethylsilylacetylenyl group at the other end. The iodo terminus of monomer **1** can couple with the terminal acetylenes under the Sonogashira reaction condition while the other terminal trimethylsilylacetylenyl group of monomer **1** can be tolerated under this reaction condition. Therefore, 2 equiv. of monomer **1** can couple with 1 equiv. of compound **2** under the Sonogashira reaction conditions and give oligomer **3** in 59% yield. The following desilylation under basic condition afford oligomer **4** in

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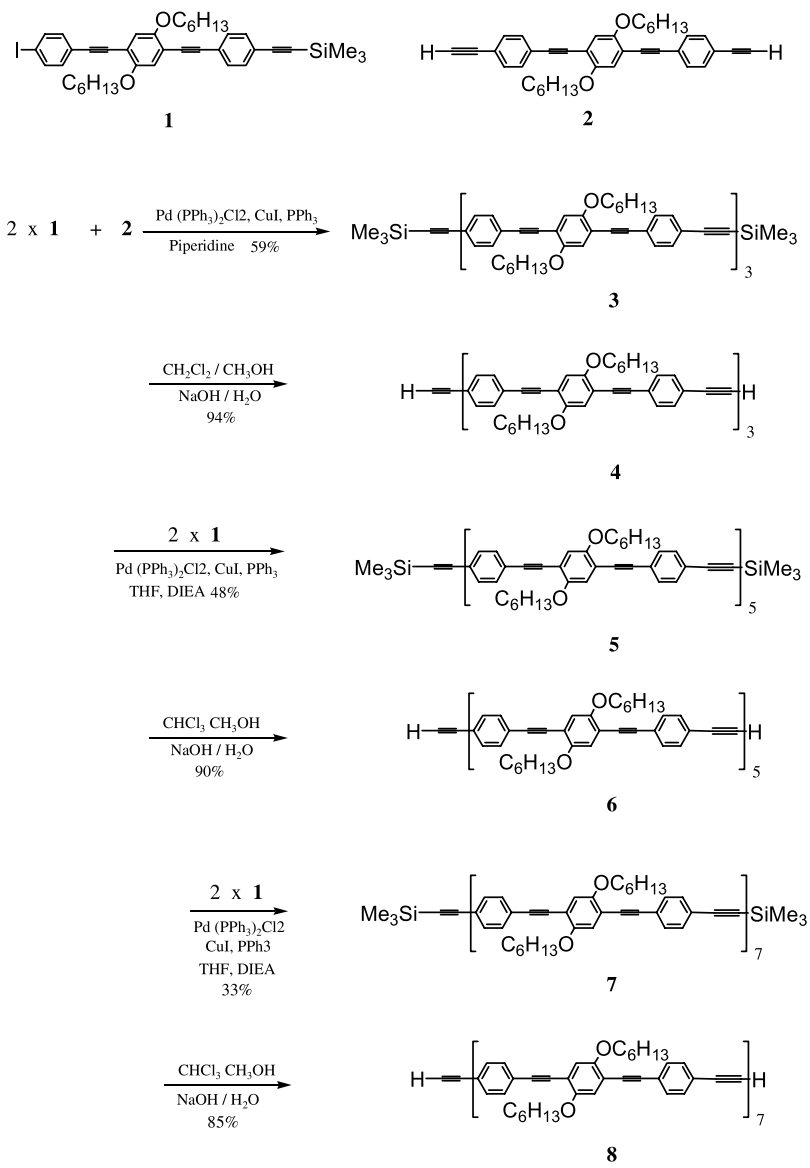
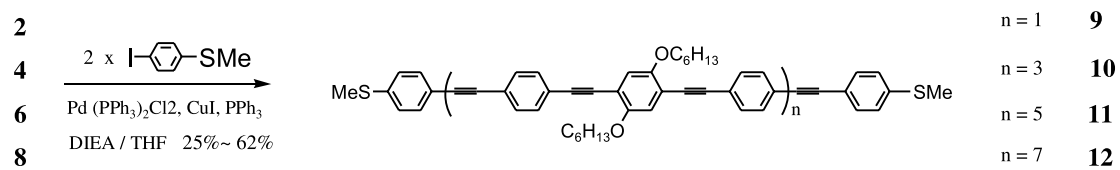


Scheme 1. Iterative coupling reaction for the synthesis of OPEs.

94% yield. Similar coupling of 1 equiv. of oligomer **4** with 3 equiv. of monomer **1** under Sonogashira reaction conditions and followed by basic desilylation successfully afford oligomer **5** and **6**, in 48 and 90% yields, respectively. Iterative coupling of 1 equiv. of oligomer **6** with 2 equiv. of monomer **1** under Sonogashira reaction conditions and followed by basic desilylation can give oligomer **7** and **8**, in 33 and 85% yields, respectively. Accordingly, the growth of OPE chain commences with compound **2** and thereafter monomer **1** is added in a repetitive stepwise fashion to add six benzene rings and six carbon–carbon triple bonds at one time. The process could be repeated to quickly build up longer OPE molecules possessing terminal acetylene groups as the functionalized termini. Oligomers **2**, **4**, **6**, and **8** with two terminal acetylene groups at the termini can further undergo Sonogashira reaction with 2 equiv. of 1-iodo-4-methylthiobenzene to form **9**–**12** in 62, 52, 31, and 24% yields, respectively (Scheme 2). It is needed to know that the introduction of masked thiol (mercapto) end-groups at the terminal positions of the oligomers can serve as an anchor groups for attachment to the gold electrode surface.[18,19] The single crystal X-ray analysis of oligomer **9** shows that the distance between the two sulfur atoms is 33.635 Å (Fig. 1).[20] In addition, when oligomers **2** and **4** were treated with 2 equiv. of *p*-iodophenylthioacetate under the Sonogashira reaction conditions, oligomers **13** and **14**



Scheme 2. Preparation of OPEs with methylsulfide as the terminal groups.

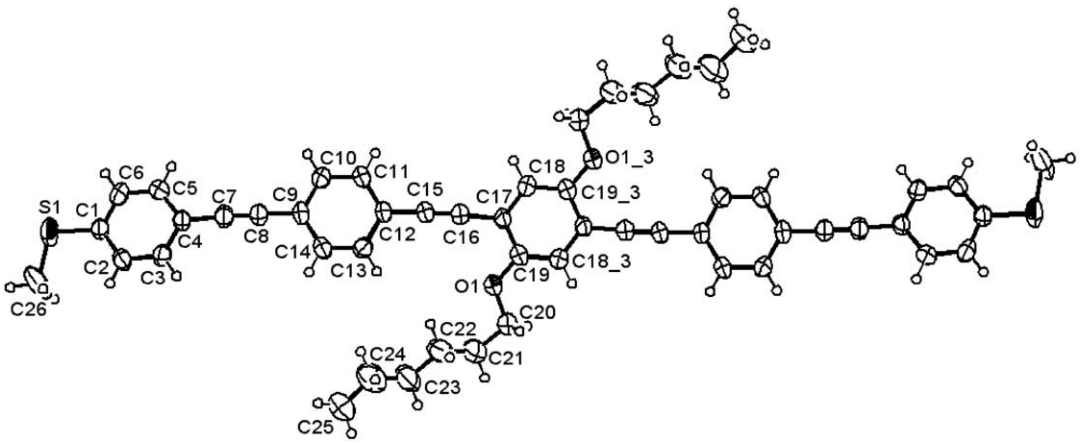
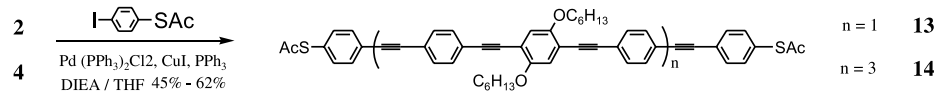
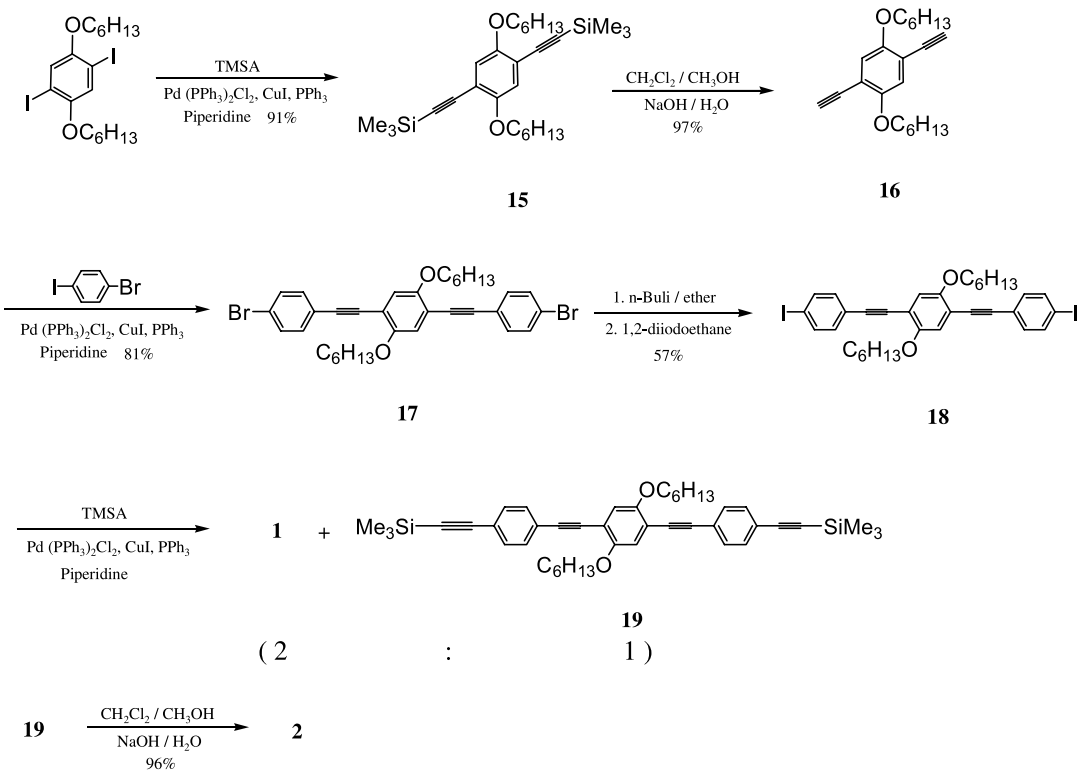


Figure 1. X-ray of compound **9**.

could be isolated in 52 and 45% yields, respectively (Scheme 3). The lower yields for the preparation of longer OPEs may due to their lower solubilities under the reaction conditions and some unknown by-products with lower R_f values on thin layer chromatography analysis using a mixture of hexane and chloroform as the mobile phase. The transformation of the terminal methylsulfide groups on **9** to the two terminal mercapto groups in good yield (>90% yield) can be done by treating **9** with 5 equiv. of sodium 2-methyl-2-propanethiolate in very dry DMF.[21] Reduced solubility of the longer oligomers poses a problem in the purification of these compounds, but analytically pure samples could be obtained through careful flash column chromatography using mixtures of chloroform and hexane as the mobile phase. Yields for each of the steps are fair to moderate with decreased solubility of the longer OPEs limiting the yields somewhat. Presently, we have succeeded in the synthesis and purification of oligomer **12**, which has 23 benzene rings and 22 triple bonds in its conjugation pathway, and a molecular weight of 3775.2238. Our success



Scheme 3. Preparation of OPEs with thioacetate as the terminal groups.



Scheme 4. Synthesis of building block molecules **1** and **2**.

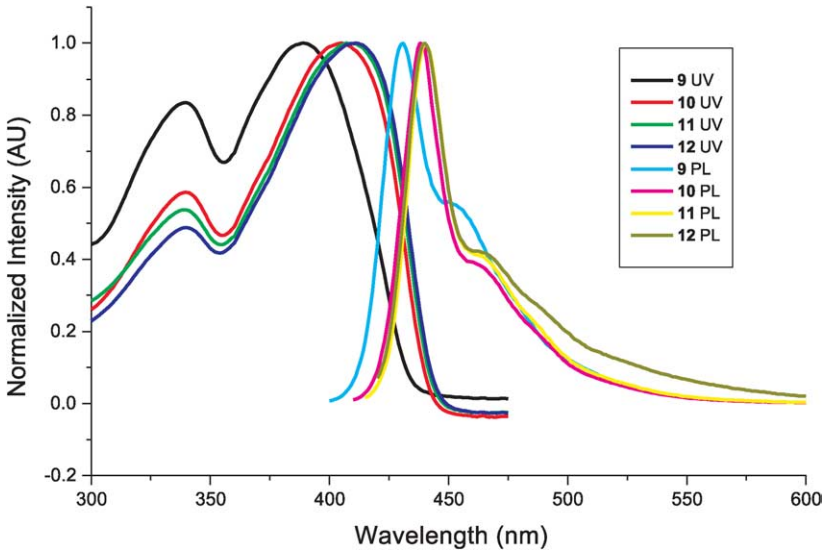


Figure 2. UV and Em of OPE oligomers **9** (5.32×10^{-6} M), **10** (4.06×10^{-6} M), **11** (3.33×10^{-6} M), and **12** (2.04×10^{-6} M) in $CHCl_3$ at 25 °C.

of preparing such a longer OPE may be due to its better solubility in the reaction solvents than most reported OPEs in their reaction solvents. The presence of the 2,5-alkoxyl groups in every three benzene rings of these OPEs may also increase their solubilities in the reaction solvents.[16] Synthesis of longer oligomers is still in progress. All of the spectroscopic studies and elemental analysis results are consistent with the proposed molecular structures.

The strategy in synthesizing the building block molecules for OPEs was shown in Scheme 4. Thus, 1,4-diiodo-2,5-dihexyloxybenzene[22] was reacted with 2 equiv. of trimethylsilylacetylene under Sonogashira reaction conditions could afford compound **15** (91% yield), which was desilylated under basic reaction conditions to give compound **16** in 97% yield. Dibromo compound **17** was prepared in 81% yield by Sonogashira coupling reaction from 1 equiv. of compound **16** and 2 equiv. of 4-bromo-1-iodobenzene in highly regioselective manner. Lithium-halogen exchange reaction followed by iodination with 1,2-diiodoethane could give diiodo compound **18** in 57% yield. Sonogashira reaction of 1 equiv. of diiodo compound **18** with 1 equiv. of trimethylsilylacetylene could afford compound **1** and compound **19** in 52 and 24% yields, respectively. The two products could be separated from the reaction mixture by flash column chromatography using a mixture of hexane and ethyl acetate as the mobile phase. An alternative approach and high yield (>93%) to the rapid synthesis of OPE molecule **19** is to react 2.2 equiv. of trimethylsilylethynyl with 1 equiv. of diiodo compound **18** under the Sonogashira reaction conditions.

The absorption and emission spectra for the series of OPEs that possess the methylthio end groups are shown in Figure 2. All of the oligomers show strong and broad absorption in the visible region. Elongation of the conjugation length from oligomer **9** to oligomer **10** results in a red shift of 16 nm (Table 1). However, only little red shift is noticed after the conjugation length reaches 11 benzene rings and 10 triple bonds. The saturation in λ_{max} has been observed previously and arises because of the limitations to electron delocalization in the longer oligomers.[23] Thus, the effective conjugation length in this series of oligomers is reached at oligomer **10**. All the four OPEs **9**–**12** showed a shorter absorption wavelength maximum at 340 nm. Elongation of the conjugation length from **9** to **12** results in a red shift of 9 nm in the emission spectra, while a red shift of 7 nm from **9** to **10** and a red shift of 2 nm from **10** to **11** and the same λ_{max} for **11** and **12** in the emission spectra. The extinction coefficients based on the oligomer molecules OPEs **9**–**12** are 1.00×10^5, 1.91×10^5, 3.07×10^5, and 4.88×10^5, respectively. It indicates that increasing the conjugation length of OPE may also increase the transition probability of electrons from their ground states to the excited states. There is a major band with a shoulder to the red of moderate intensity in the emission spectrum of OPEs **9**–**12**. It is noteworthy that the half bandwidths of the emission spectra of OPEs **9**–**12** are much narrow as compared with that of OPVs.[16] At present, it is not clear why this should be the case. No change in any of the emission spectra was observed when fluorescence measurements were made over a wide range of concentrations ($2\times10^{-5}-5\times10^{-8}$ M), suggesting that excimer formation does not occur. The fluorescence quantum yields of the OPEs **9** to **12** in dichloromethane are 80, 77, 77, and 63%, respectively (Table 1). It is interesting to note that the quantum yields are decreased as the conjugation length increases.

Table 1. The absorption λ_{max} (in $CHCl_3$), extinction co-efficiency, emission λ_{max} (in $CHCl_3$), and fluorescent quantum yield of OPEs

Oligomer	UV λ_{max} (nm)	$\varepsilon\times10^{-5}$	Em λ_{max} (nm)	Φ_F[a]
9	389	1.00	431	0.80
10	405	1.91	438	0.77
11	407	3.07	440	0.77
12	411	4.88	440	0.63

[a] Use *p*-distyrylbenzene ($\Phi_F\cong0.9$) to compare with in dichloromethane.[24]

It should be pointed out that various syntheses of different OPEs have been reported in the past.[25–28] Tour et al. have reported the improved and new synthesis of OPE molecules with nitro groups and with nitrile group as the alligator clip to a metal surface as the potential molecular electronic

devices.[25] Their rapid bi-directional synthesis of OPEs containing with or without thienyl rings or the solid phase synthesis of OPEs are also noteworthy.[1,26] Godt et al. have applied the iterative convergent/divergent strategy based on the bromine–iodine selectivity of the palladium-catalyzed alkyne-aryl coupling reactions to form OPEs with 9 mer.[27] Meier et al. have investigated the non-linear optics of monodisperse OPEs with up to 6 mer.[28] The work presented in this paper is distinct from others in that our approach is open ended and very versatile, and it enables us to synthesize longer oligomers that more closely resemble organic polymeric conducting materials. Due to the fact that the Sonogashira reaction tolerates a wide variety of functional groups,[18,19] it should be possible to synthesize many different OPE molecules of various lengths and structures. This is useful for fine-tuning the band gap in emissive organic materials. Also noteworthy is the use of only one reaction type to construct the whole molecules. The use of building blocks with three benzene rings allows for efficient and fast construction of the OPE chain. After desilylation steps, two terminal acetylene functional groups are left for further chemical manipulation which may include either continued elongation or reaction with an end-functionalized polymer to form novel diblock copolymers or with an end-capped monomer to form longer oligomers. Controlled bidirectional growth is also possible, enabling a very rapid construction of OPEs possessing various functional groups at both ends. Thus, we can use the iterative coherent approach to effectively and rapidly synthesize longer OPEs.

In summary, our general and controlled bidirectional growth strategy enables a very rapid and efficient construction of OPEs possessing functional groups at both ends. So far, we can prepare oligomer **12**, which has 23 benzene rings and 22 triple bonds in its conjugation system. The strategy employs only one reaction type to grow the conjugated chains. We intend to use these molecules in the production of novel molecular wires.

3. Experimental

3.1. General

All reactions were carried out under an atmosphere of nitrogen. Tetrahydrofuran (THF) was dealt with dried NaH and then distilled over sodium/benzophenone ketyl whenever 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. Melting points (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, 400 or 500 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 $CHCl_3$ solution unless otherwise stated.

3.1.1. 1,4-Bis-hexyloxy-2,5-bis-trimethylsilylethynylbenzene 15. To a dried round-bottomed flask were added 1,4-bis-hexyloxy-2,5-diiodobenzene[22] (10.0 g, 18.87 mmol), bis(triphenylphosphine)palladium dichloride (0.52 g, 0.74 mmol), copper(I) iodide (0.28 g, 1.47 mmol), triphenylphosphine (0.77 g, 2.94 mmol). The system was evacuated and flushed with nitrogen (3×) and the dry piperidine (50 mL) was degassed with nitrogen and then added. Under stirring, trimethylsilylacetylene (3.71 g, 37.85 mmol) was added to solution. The mixture was stirred at rt for 6 h. The solvent was evaporated, and chloroform was added. The organic phase was washed with saturated solution of NH_4Cl (3×50 mL), solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was purified by column chromatography (silica gel, hexane/chloroform, 10:0.5) to give the compound **15** as white solid (8.09 g, 91% yield). Mp 75–76 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.25 (s, 18H), 0.90 (t, J=7 Hz, 6H), 1.30–1.35 (m, 8H), 1.47–1.52 (m, 4H), 1.75–1.80 (m, 4H), 3.94 (t, J=7 Hz, 4H), 6.88 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.03, 14.17, 22.72, 25.77, 29.37, 31.69, 69.49, 100.15, 101.13, 113.98, 117.23, 154.07 ppm; IR ($CHCl_3$) ν 2137, 1269, 1015 cm^{-1}; MS (m/z) 470.2 (M^+); HRMS calcd for $C_{28}H_{46}O_2Si_2$ 470.3036, found 470.3032.

3.1.2. 1,4-Diethynyl-2,5-bis-hexyloxybenzene 16. Compound **15** (8.0 g, 16.98 mmol) was dissolved in $CHCl_3$ (50 mL), CH_3OH (10 mL) and solution of NaOH (2.7 g, 67.5 mol) in 10 mL of water were added. The mixture was stirred at rt for 12 h, and then washed with saturated solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was recrystallized from $CHCl_3$/hexane to provide pure compound **16** as white solid (5.32 g, 97% yield). Mp 70–71 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J=7 Hz, 6H), 1.33–1.35 (m, 8H), 1.42–1.47 (m, 4H), 1.75–1.84 (m, 4H), 3.34 (s, 2H), 3.97 (t, J=7 Hz, 4H), 6.95 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.93, 22.50, 25.50, 29.00, 31.44, 69.52, 79.70, 82.37, 113.16, 117.60, 153.89 ppm; IR ($CHCl_3$) ν 2106, 1269, 1015 cm^{-1}. MS (m/z) 326.3 (M^+); HRMS calcd for $C_{22}H_{30}O_2$ 326.2246, found 326.2254.

3.1.3. 1,4-Bis-(4-bromo-phenylethynyl)-2,5-bis-hexyloxybenzene 17. To a dried round-bottomed flask were added compound **16** (5.0 g, 15.31 mmol), 1-bromo-4-iodobenzene (8.67 g, 30.64 mmol), bis(triphenylphosphine)-palladium dichloride (0.43 g, 0.61 mmol), copper(I) iodide (0.23 g, 1.21 mmol), triphenylphosphine (0.63 g, 2.40 mmol). The system was evacuated and flushed with nitrogen (3×), the dry piperidine (60 mL) was degassed with nitrogen and then added into the reaction mixture. The mixture was stirred at rt for 8 h. The solvent was evaporated, and chloroform was added. The organic phase was washed

with saturated solution of NH_4Cl (3×50 mL), solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was purified by column chromatography (silica gel, hexane/chloroform, 10:0.5) to give compound **17** as faint yellow solid (7.89 g, 81% yield). Mp 112–113 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J=7 Hz, 6H), 1.33–1.37 (m, 8H), 1.51–1.56 (m, 4H), 1.79–1.86 (m, 4H), 4.02 (t, J=7 Hz, 4H), 6.70 (s, 2H), 7.39 (d, J=8 Hz, 4H), 7.49 (d, J=8 Hz, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.02, 22.62, 25.70, 29.24, 31.56, 69.54, 87.05, 93.82, 113.78, 116.72, 122.35, 122.49, 131.57, 132.92, 153.60 ppm; IR ($CHCl_3$) ν 2209, 1274, 1186, 1067 cm^{-1}; MS (m/z) 634 (M^+); HRMS calcd for $C_{34}H_{36}O_2Br_2$ 634.1082, found 634.1096.

3.1.4. 1,4-Bis-hexyloxy-2,5-bis(4-iodo-phenylethynyl)-benzene 18. To a dried two-neck round-bottomed flask was added compound **17** (10 g, 15.72 mmol), the system was evacuated and flushed with nitrogen. Dry ether (200 mL) was added, and solution of *n*-BuLi (2.5 M, 12.6 mL) in ether (100 mL) was then added dropwise at 0 °C. After stirring at 0 °C for 3 h, the solution of 1,2-diiodoethane (8.90 g, 31.56 mmol) in 20 mL of ether was added, the reaction mixture was stirred at rt for 12 h. The solution was then washed with saturated solution of $Na_2S_2O_3$ (2×50 mL), solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum, the crude product was purified by column chromatography (silica gel, hexane/$CHCl_3$=5:0.5) to give compound **18** as a light yellow solid (6.5 g, 57% yield). Mp 110–111 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J=7 Hz, 6H), 1.29–1.36 (m, 8H), 1.47–1.54 (m, 4H), 1.78–1.97 (m, 4H), 4.01 (t, J=7 Hz, 4H), 6.98 (s, 2H), 7.24 (d, J=8 Hz, 4H), 7.67 (d, J=8 Hz, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.05, 22.63, 25.72, 29.25, 31.57, 69.56, 87.35, 94.00, 94.16, 113.80, 116.74, 122.92, 133.01, 137.49, 153.61 ppm; IR ($CHCl_3$) ν 2199, 1274, 1212, 1051 cm^{-1}; MS (m/z) 730 (M^+); HRMS calcd for $C_{34}H_{36}O_2I_2$ 730.0805, found 730.0811.

3.1.5. {4-[2,5-Bis-hexyloxy-4-(4-iodo-phenylethynyl)-phenylethynyl]phenylethynyl}-tri-methylsilane 1 and 1,4-bis-hexyloxy-2,5-bis(4-trimethylsilanylethynyl-phenyl-ethynyl)benzene 19. To a dried round-bottomed flask were added compound **18** (5.0 g, 6.85 mmol), bis(triphenylphosphine)palladium dichloride (0.11 g, 0.16 mmol), copper(I) iodide (0.06 g, 0.32 mmol), triphenylphosphine (0.16 g, 0.61 mmol). The system was evacuated and flushed with nitrogen (3×), the dry piperidine (30 mL) was degassed with nitrogen and then added into the reaction mixture. Under stirring, trimethylsilylacetylene (0.68 g, 6.94 mmol) was added to the solution. The mixture was stirred at rt for 3 h. The solvent was evaporated, and chloroform was added. The organic phase was washed with saturated solution of NH_4Cl (3×50 mL), solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was separated by column chromatography (silica gel, hexane/chloroform, 10:0.5–1) to give the unreacted compound **18** (1.2 g), compound **1** (2.51 g), and compound **19** (1.1 g).

Compound **1**. Yellow solid (2.51 g, 52% yield). Mp 98–99 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 9H), 0.90 (t, J=7 Hz, 6H), 1.30–1.35 (m, 8H), 1.51–1.56 (m, 4H), 1.79–1.86 (m, 4H), 4.02 (t, J=7 Hz, 4H), 6.99 (s, 2H), 7.24 (d, J=8 Hz, 4H), 7.45 (s, 4H), 7.68 (d, J=8 Hz, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.10, 14.03, 22.62, 25.71, 29.25, 31.56, 69.55, 69.58, 87.38, 87.88, 93.97, 94.12, 94.61, 96.31, 104.65, 113.75, 113.93, 116.76, 122.87, 122.94, 123.45, 131.31, 131.85, 133.00, 137.48, 153.62 ppm; IR ($CHCl_3$) ν 2147, 1274, 1248, 1191 cm^{-1}; MS (m/z) 700 (M^+); HRMS calcd for $C_{39}H_{45}O_2SiI$ 700.2234, found 700.2227.

Compound **19**. Yellow solid (1.10 g, 24% yield). Mp 156–157 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 18H), 0.90 (t, J=7 Hz, 6H), 1.34–1.38 (m, 8H), 1.52–1.54 (m, 4H), 1.82–1.87 (m, 4H), 4.02 (t, J=7 Hz, 4H), 7.00 (s, 2H), 7.45 (s, 8H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.10, 14.03, 22.63, 25.73, 29.26, 31.58, 59.57, 87.91, 94.60, 96.29, 104.66, 113.87, 116.77, 122.85, 123.47, 131.31, 131.85, 153.63 ppm; IR ($CHCl_3$) ν 2147, 1409, 1378, 1020 cm^{-1}; MS (m/z) 670.4 (M^+); HRMS calcd for $C_{44}H_{54}O_2Si_2$ 670.3662, found 670.3652.

The compound **19** can also be obtained in 96% yield by reaction of compound **18** and 2.0 equiv. of trimethylsilylacetylene.

3.1.6. 1,4-Bis-(4-ethynyl-phenylethynyl)-2,5-bis-hexyl-oxy-benzene 2. Compound **19** (2.0 g, 2.98 mmol) was dissolved in $CHCl_3$ (50 mL), CH_3OH (10 mL) and solution of NaOH (0.96 g, 24.0 mol) in 10 mL of water were added. The mixture was stirred at rt for 12 h, and then washed with saturated solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was recrystallized from $CHCl_3$/hexane to provide pure compound **2** as yellow solid (1.50 g, 96% yield). Mp 112–114 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J=7 Hz, 6H), 1.31–1.36 (m, 8H), 1.50–1.58 (m, 4H), 1.80–1.87 (m, 4H), 3.18 (s, 2H), 4.03 (t, J=7 Hz, 4H), 7.01 (s, 2H), 7.47 (s, 8H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.01, 22.62, 25.72, 29.25, 31.57, 69.55, 78.93, 83.28, 87.97, 94.39, 113.84, 116.76, 121.83, 123.89, 131.38, 132.01, 153.65 ppm; IR ($CHCl_3$) ν 2099, 1284, 1017 cm^{-1}; MS (m/z) 526 (M^+); HRMS calcd for $C_{38}H_{38}O_2$ 526.2872, found 526.2866.

Oligomer **3**. To a dried round-bottomed flask were added compound **1** (1.73 g, 2.47 mmol), compound **2** (0.65 g, 1.23 mmol), bis(triphenylphosphine)palladium dichloride (0.04 g, 0.06 mmol), copper(I) iodide (0.02 g, 0.11 mmol), triphenylphosphine (0.06 g, 0.23 mmol). The system was evacuated and flushed with nitrogen (3×), the dry piperidine (50 mL) was degassed with nitrogen and then added. The mixture was stirred at rt for 12 h. The solvent was evaporated, and chloroform was added. The organic phase was washed with saturated solution of NH_4Cl (3×50 mL), solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was purified by column chromatography (silica gel, hexane/chloroform, 10:6) to give the oligomer **3** as yellow solid (1.22 g, 59% yield). Mp 146–147 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 18H), 0.85–0.92 (t, J=7 Hz, 18H), 1.30–1.37 (m, 24H), 1.55–1.58 (m, 12H), 1.83–1.87 (m, 12H), 4.03 (t, J=7 Hz, 12H), 7.02 (s, 6H), 7.45 (s, 8H), 7.52 (s,

16H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.09, 14.04, 22.64, 25.75, 29.29, 31.60, 69.61, 87.92, 88.06, 91.08, 94.67, 96.31, 104.68, 113.93, 116.81, 122.82, 123.48, 131.33, 131.52, 131.87, 132.41, 153.67 ppm; IR ($CHCl_3$) ν 2135, 1277, 1019 cm^{-1}; MS (*m*/*z*) 1670.5 (M^+); HRMS calcd for $C_{116}H_{126}O_6Si_2$ 1670.9093, found 1670.9072.

Oligomer **4**. Oligomer **3** (1.0 g, 0.60 mmol) was dissolved in $CHCl_3$ (60 mL), CH_3OH (10 mL) and solution of NaOH (0.3 g, 7.5 mol) in 10 mL of water were added. The mixture was stirred at 50 °C for 15 h, and then washed with saturated solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was recrystallized from $CHCl_3$/hexane to provide pure oligomer **4** as yellow solid (0.86 g, 94% yield). Mp 117–119 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86–0.93 (m, 18H), 1.30–1.37 (m, 24H), 1.52–1.55 (m, 12H), 1.84–1.88 (m, 12H), 3.18 (s, 2H), 4.04 (m, 12H), 7.02 (s, 6H), 7.47 (s, 8H), 7.52 (s, 16H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.05, 22.65, 25.75, 29.30, 31.60, 69.62, 78.92, 83.32, 88.06, 91.09, 94.42, 94.70, 113.97, 116.86, 121.85, 122.83, 123.48, 123.93, 131.41, 131.53, 132.05, 153.69 ppm; IR ($CHCl_3$) ν 2099, 1280, 1015 cm^{-1}; MS (*m*/*z*) 1527.1 (M^+); HRMS calcd for $C_{110}H_{110}O_6$ 1526.8302, found 1526.8350.

Oligomer **5**. To a dried round-bottomed flask were added compound **1** (0.80 g, 1.14 mmol), bis(triphenylphosphine)-palladium dichloride (0.04 g, 0.06 mmol), copper(I) iodide (0.02 g, 0.11 mmol), triphenylphosphine (0.06 g, 0.23 mmol). The system was evacuated and flushed with nitrogen (3×), THF (20 mL) and DIEA (20 mL) were degassed with nitrogen and then added. Compound **4** (0.95 g, 0.57 mmol) was evacuated and flushed with nitrogen (3×) in another dried round-bottomed flask, and dissolved in degassed THF (25 mL), and then added above system. The mixture was stirred at rt for 12 h and then at 50 °C for 8 h. The solvent was evaporated, and chloroform was added. The organic phase was washed with saturated solution of NH_4Cl (3×50 mL), solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was purified by column chromatography (silica gel, hexane/chloroform, 10:6) to give the oligomer **5** as yellow solid (0.73 g, 48% yield). Mp 188–189 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 18H), 0.89–0.94 (m, 30H), 1.35–1.39 (m, 40H), 1.53–1.56 (m, 20H), 1.84–1.89 (m, 20H), 4.01–4.07 (m, 20H), 7.01–7.02 (m, 10H), 7.45 (s, 8H), 7.52 (s, 32H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.10, 14.05, 22.65, 25.75, 29.29, 31.60, 69.61, 87.93, 88.07, 91.08, 94.68, 96.31, 104.67, 113.93, 116.80, 122.82, 123.48, 131.32, 131.52, 131.86, 153.68 ppm; IR ($CHCl_3$) ν 2145, 1279, 1020 cm^{-1}; MS (*m*/*z*) 2671.8 (M^+); HRMS calcd for $C_{188}H_{198}O_{10}Si_2$ 2671.4524, found 2671.4532.

Oligomer **6**. Oligomer **5** (0.80 g, 0.30 mmol) was dissolved in $CHCl_3$ (70 mL), CH_3OH (10 mL) and solution of NaOH (0.3 g, 7.5 mol) in 10 mL of water were added. The mixture was stirred at 75 °C for 24 h, and then washed with saturated solution of NaCl (3×50 mL), dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was recrystallized from $CHCl_3$/hexane to provide pure oligomer **6** as yellow solid (0.68 g, 90% yield). Mp 146–147 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83–0.97 (m, 30H), 1.35–1.42 (m, 40H), 1.53–1.57 (m, 20H), 1.84–1.91 (m, 20H), 3.18 (s, 2H), 4.02–4.07 (m, 20H), 7.02 (s, 10H), 7.47 (s, 8H), 7.52 (s, 32H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.16, 22.76, 25.87, 29.42, 31.72, 69.76, 79.02, 83.43, 88.20, 91.21, 94.53, 94.81, 114.08, 116.97, 121.97, 122.95, 123.61, 124.06, 131.53, 131.64, 132.16, 153.82 ppm; IR ($CHCl_3$) ν 2101, 1282, 1017 cm^{-1}; MS (*m*/*z*) 2527.5 (M^+); HRMS calcd for $C_{182}H_{182}O_{10}$ 2527.3733, found 2527.3742.

Oligomer **7**. To a dried round-bottomed flask were added compound **1** (0.36 g, 0.51 mmol), bis(triphenylphosphine)-palladium dichloride (0.02 g, 0.03 mmol), copper(I) iodide (0.01 g, 0.05 mmol), triphenylphosphine (0.03 g, 0.11 mmol). The system was evacuated and flushed with nitrogen (3×), THF (20 mL) and DIEA (20 mL) were degassed with nitrogen and then added. Compound **6** (0.65 g, 0.26 mmol) was evacuated and flushed with nitrogen (3×) in another dried round-bottomed flask, and dissolved in degassed THF (35 mL), and then added above system. The mixture was stirred at 50 °C for 24 h. The solvent was evaporated, and chloroform was added. The organic phase was washed with saturated solution of NH_4Cl (3×50 mL), solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was purified by column chromatography (silica gel, hexane/chloroform, 10:6) to give the oligomer **7** as yellow solid (0.31 g, 33% yield). Mp 176–177 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 18H), 0.83–0.97 (m, 42H), 1.35–1.43 (m, 56H), 1.53–1.58 (m, 28H), 1.84–1.91 (m, 28H), 4.03–4.07 (m, 28H), 7.02 (s, 14H), 7.45 (s, 8H), 7.52 (s, 48H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.10, 14.05, 22.65, 25.75, 29.29, 31.60, 69.60, 88.06, 91.08, 94.68, 96.30, 104.65, 113.91, 116.79, 122.81, 123.47, 131.32, 131.51, 131.86, 153.67 ppm; IR ($CHCl_3$) ν 2145, 1278, 1019 cm^{-1}; MS (*m*/*z*) 3671.5 (M^+); HRMS calcd for $C_{260}H_{270}O_{14}Si_2$ 3671.9954, found 3671.9962.

Oligomer **8**. Oligomer **7** (0.60 g, 0.16 mmol) was dissolved in $CHCl_3$ (80 mL), CH_3OH (10 mL) and solution of NaOH (0.15 g, 3.75 mol) in 10 mL of water were added. The mixture was stirred at 75 °C for 35 h, and then washed with saturated solution of NaCl (3×50 mL), dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was recrystallized from $CHCl_3$/hexane to provide pure oligomer **8** as yellow solid (0.49 g, 85% yield). Mp 155–156 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89–0.93 (m, 42H), 1.35–1.43 (m, 56H), 1.54–1.59 (m, 28H), 1.82–1.91 (m, 28H), 3.18 (s, 2H), 4.03–4.07 (m, 28H), 7.02 (s, 14H), 7.47 (s, 8H), 7.52 (s, 48H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.16, 22.76, 25.87, 29.42, 31.72, 69.75, 79.01, 83.42, 88.19, 91.21, 94.53, 94.81, 114.06, 116.96, 121.96, 122.94, 123.61, 124.05, 131.52, 131.64, 132.16, 153.81 ppm; IR ($CHCl_3$) ν 2101, 1280, 1015 cm^{-1}; MS (*m*/*z*) 3527.7 (M^+); HRMS calcd for $C_{254}H_{254}O_{14}$ 3527.9164, found 3527.9172.

3.1.7. 1,4-Bis-hexyloxy-2,5-bis-[4-(4-methylsulfanyl-phenylethynyl)-phenylethynyl]-benzene 9. To a dried round-bottomed flask were added compound **2** (0.50 g, 0.95 mmol), 1-iodo-4-methylsulfanyl-benzene (0.48 g, 1.92 mmol), bis(triphenylphosphine)-palladium dichloride (0.03 g, 0.04 mmol), copper(I) iodide (0.02 g, 0.11 mmol), triphenylphosphine (0.06 g, 0.23 mmol). The system was evacuated and flushed with nitrogen (3×), the dry piperidine

(30 mL) was degassed with nitrogen and then added. The mixture was stirred at rt for 10 h. The solvent was evaporated, and chloroform was added. The organic phase was washed with saturated solution of NH_4Cl (3×50 mL), solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was purified by column chromatography (silica gel, hexane/chloroform, 10:4) to give the oligomer **9** as yellow solid (0.45 g, 62% yield). This oligomer **9** can be further purified by recrystallization from $CHCl_3$ to give crystals for X-ray analysis. Mp 187–188 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J=7 Hz, 6H), 1.35–1.39 (m, 8H), 1.53–1.58 (m, 4H), 1.84–1.88 (m, 4H), 2.51 (s, 6H), 4.04 (t, J=7 Hz, 4H), 7.02 (s, 2H), 7.22 (d, J=8 Hz, 4H), 7.45 (d, J=8 Hz, 4H), 7.50 (s, 8H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.05, 15.32, 22.65, 25.75, 29.29, 31.60, 69.60, 87.88, 89.27, 91.17, 94.73, 113.91, 116.80, 119.24, 123.11, 123.15, 125.81, 131.42, 131.48, 131.87, 139.64, 153.65 ppm; IR ($CHCl_3$) ν 2212, 1275, 1089, 1011 cm^{-1}; MS (*m*/*z*): 770 (M^+); HRMS calcd for $C_{52}H_{50}O_2S_2$ 770.3252, found 770.3251.

Oligomer **10**. To a dried round-bottomed flask were added 1-iodo-4-methylsulfanyl-benzene (0.13 g, 0.52 mmol), bis(triphenyl-phosphine)palladium dichloride (0.02 g, 0.03 mmol), copper(I) iodide (0.01 g, 0.05 mmol), triphenylphosphine (0.03 g, 0.11 mmol). The system was evacuated and flushed with nitrogen (3×), THF (10 mL) and DIEA (15 mL) were degassed with nitrogen and then added. Compound **4** (0.40 g, 0.26 mmol) was evacuated and flushed with nitrogen (3×) in another dried round-bottomed flask, and dissolved in degassed THF (20 mL), and then added above system. The mixture was stirred at rt 8 h and at 50 °C for 6 h. The solvent was evaporated, and chloroform was added. The organic phase was washed with saturated solution of NH_4Cl (3×50 mL), solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was purified by column chromatography (silica gel, hexane/chloroform, 10:6) to give the oligomer **10** as yellow solid (0.24 g, 52% yield). Mp 179–180 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J=7 Hz, 18H), 1.26–1.38 (m, 24H), 1.51–1.63 (m, 12H), 1.82–1.91 (m, 12H), 2.51 (s, 6H), 4.05 (t, J=7 Hz, 12H), 7.02 (s, 6H), 7.22 (d, J=8 Hz, 4H), 7.44 (d, J=8 Hz, 4H), 7.50 (s, 8H), 7.52 (s, 16H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.05, 15.32, 22.65, 25.75, 29.29, 31.60, 69.61, 87.88, 88.07, 89.27, 91.09, 91.18, 94.67, 94.77, 113.86, 113.92, 113.98, 116.81, 119.24, 122.82, 123.14, 123.48, 125.82, 131.42, 131.48, 131.52, 131.87, 139.65, 153.68 ppm; IR ($CHCl_3$) ν 2210, 1276, 1088, 1011 cm^{-1}; MS (*m*/*z*) 1771 (M^+); HRMS calcd for $C_{124}H_{122}O_6S_2$1770.8682, found 1770.8695.

Oligomer **11**. To a dried round-bottomed flask were added 1-iodo-4-methylsulfanyl-benzene (0.10 g, 0.40 mmol), bis(triphenylphosphine)palladium dichloride (0.02 g, 0.03 mmol), copper(I) iodide (0.01 g, 0.05 mmol), triphenylphosphine (0.03 g, 0.11 mmol). The system was evacuated and flushed with nitrogen (3×), THF (10 mL) and DIEA (15 mL) were degassed with nitrogen and then added. Compound **6** (0.50 g, 0.20 mmol) was evacuated and flushed with nitrogen (3×) in another dried round-bottomed flask, and dissolved in degassed THF (20 mL), and then added above system. The mixture was stirred at rt for 8 h and at 50 °C for another 6 h. The solvent was evaporated, and chloroform was added. The organic phase was washed with saturated solution of NH_4Cl (3×50 mL), solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was purified by column chromatography (silica gel, hexane/chloroform, 10:8) to give the oligomer **11** as yellow solid (0.17 g, 31% yield). Mp 167–168 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83–0.95 (m, 30H), 1.32–1.38 (m, 40H), 1.51–1.58 (m, 20H), 1.82–1.91 (m, 20H), 2.51 (s, 6H), 4.05 (t, J=7 Hz, 20H), 7.02 (s, 10H), 7.22 (d, J=8 Hz, 4H), 7.44 (d, J=8 Hz, 4H), 7.50 (s, 8H), 7.52 (s, 32H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.03, 15.31, 22.63, 25.73, 29.28, 31.58, 69.60, 87.86, 88.05, 89.25, 91.07, 94.67, 113.90, 116.78, 119.23, 122.80, 123.12, 123.46, 125.80, 131.40, 131.50, 131.85, 139.63, 153.66 ppm; IR ($CHCl_3$) ν 2210, 1276, 1089, 1010 cm^{-1}; MS (*m*/*z*) 2771.7 (M^+); HRMS calcd for $C_{196}H_{194}O_{10}S_2$ 2771.4113, found 2771.4122.

Oligomer **12**. To a dried round-bottomed flask were added 1-iodo-4-methylsulfanyl-benzene (0.05 g, 0.20 mmol), bis(triphenyl-phosphine)palladium dichloride (0.02 g, 0.03 mmol), copper(I) iodide (0.01 g, 0.05 mmol), triphenylphosphine (0.03 g, 0.11 mmol). The system was evacuated and flushed with nitrogen (3×), THF (10 mL) and DIEA (15 mL) were degassed with nitrogen and then added. Compound **8** (0.35 g, 0.10 mmol) was evacuated and flushed with nitrogen (3×) in another dried round-bottomed flask, and dissolved in degassed THF (20 mL), and then added above system. The mixture was stirred at 50 °C for 30 h. The solvent was evaporated, and chloroform was added. The organic phase was washed with saturated solution of NH_4Cl (3×50 mL), solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was purified by column chromatography (silica gel, hexane/chloroform, 10:6) to give the oligomer **12** as yellow solid (0.09 g, 24% yield). Mp 175–176 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83–0.95 (m, 42H), 1.32–1.38 (m, 56H), 1.51–1.58 (m, 28H), 1.82–1.91 (m, 28H), 2.51 (s, 6H), 4.05 (t, J=7 Hz, 28H), 7.02 (s, 14H), 7.22 (d, J=8 Hz, 4H), 7.44 (d, J=8 Hz, 4H), 7.50 (s, 8H), 7.52 (s, 48H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.04, 15.31, 22.64, 25.74, 29.28, 31.59, 69.59, 88.05, 91.07, 94.67, 113.90, 116.79, 122.80, 123.11, 123.46, 125.80, 131.51, 131.85, 139.63, 153.66 ppm; IR ($CHCl_3$) ν 2210, 1082, 1012 cm^{-1}; MS (*m*/*z*) 3772 (M^+); HRMS calcd for $C_{268}H_{266}O_{14}S_2$ 3771.9544, found 3771.9552.

3.1.8. Thioacetic acid *S*-[4-(4-{4-[4-(4-acetylsulfanyl-phenylethynyl)-phenylethynyl]-2,5-bis-hexyloxyl-phenylethynyl}phenylethynyl)phenyl]ester 13. To a dried round-bottomed flask were added 1-(4-iodo-phenylthio)ethan-1-one (0.42 g, 1.51 mmol), bis(triphenyl-phosphine)palladium dichloride (0.05 g, 0.07 mmol), copper(I) iodide (0.03 g, 0.16 mmol), triphenylphosphine (0.08 g, 0.31 mmol). The system was evacuated and flushed with nitrogen (3×), THF (10 mL) and DIEA (10 mL) were degassed with nitrogen and then added. Compound **2** (0.40 g, 0.76 mmol) was evacuated and flushed with nitrogen (3×) in another dried round-bottomed flask, and dissolved in degassed THF (10 mL), and then added above system. The mixture was stirred at rt for 12 h. The solvent was evaporated, and chloroform was added. The organic

phase was washed with saturated solution of NH_4Cl (3×50 mL), solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was purified by column chromatography (silica gel, hexane/chloroform, 10:4) to give the oligomer **13** as yellow solid (0.33 g, 52% yield). Mp 165–166 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J=7 Hz, 6H), 1.35–1.40 (m, 8H), 1.53–1.56 (m, 4H), 1.81–1.88 (m, 4H), 2.44 (s, 6H), 4.04 (t, J=7 Hz, 4H), 7.02 (s, 2H), 7.40 (d, J=8 Hz, 4H), 7.51 (s, 8H), 7.55 (d, J=8 Hz, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.04, 22.64, 25.74, 29.29, 30.27, 31.59, 69.62, 88.09, 90.49, 90.79, 94.66, 113.94, 116.83, 122.67, 123.58, 124.28, 128.28, 131.50, 131.58, 132.16, 134.22, 153.69, 193.38 ppm; IR ($CHCl_3$) ν 2201, 1701, 1213, 1120, 1016 cm^{-1}; MS (*m*/*z*) 826 (M^+); HRMS calcd for $C_{54}H_{50}O_4S_2$ 826.3151, found 826.3157.

Oligomer **14**. To a dried round-bottomed flask were added 1-(4-iodophenylthio)-ethan-1-one (0.21 g, 0.76 mmol), bis(triphenylphosphine)palladium dichloride (0.03 g, 0.04 mmol), copper(I) iodide (0.02 g, 0.11 mmol), triphenylphosphine (0.08 g, 0.15 mmol). The system was evacuated and flushed with nitrogen (3×), THF (10 mL) and DIEA (15 mL) were degassed with nitrogen and then added. Compound **4** (0.58 g, 0.38 mmol) was evacuated and flushed with nitrogen (3×) in another dried round-bottomed flask, and dissolved in degassed THF (20 mL), and then added above system. The mixture was stirred at rt for 12 h. The solvent was evaporated, and chloroform was added. The organic phase was washed with saturated solution of NH_4Cl (3×50 mL), solution of NaCl (3×50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum, and residue was purified by column chromatography (silica gel, hexane/chloroform, 10:4) to give the oligomer **14** as yellow solid (0.31 g, 45% yield). Mp 167–168 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88–0.93 (m, 18H), 1.32–1.38 (m, 24H), 1.54–1.56 (m, 12H), 1.82–1.91 (m, 12H), 2.44 (s, 6H), 4.05 (m, 12H), 7.02 (s, 6H), 7.41 (d, J=8 Hz, 4H), 7.52 (s, 24H), 7.56 (d, J=8 Hz, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.05, 22.65, 25.75, 29.29, 30.29, 31.60, 69.61, 88.07, 90.48, 90.79, 91.08, 94.69, 113.92, 116.80, 122.67, 122.82, 123.47, 123.57, 124.28, 128.26, 131.52, 131.59, 132.17, 134.24, 153.68, 193.46 ppm; IR ($CHCl_3$) ν 2201, 1705, 1212, 1016 cm^{-1}; MS (*m*/*z*) 1827 (M^+); HRMS calcd for $C_{126}H_{122}O_8S_2$ 1826.8581, found 1826.8589.

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