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π-EXPANDED CYCLIC OLIGOTHIOPHENE 12-MERS AS SEMISHAPE-PERSISTENT MACROCYCLES

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Dedicated to Professor Masakatsu Shibasaki on the occasion of his 70th birthday

Abstract – π-Expanded macrocyclic oligothiophene 12-mer *E,E*-**12T10A**, 18-mer *E,E,E*-**18T15A**, and 24-mer *E,E,E,E*-**24T20A** composed of thienylene, ethynylene, and vinylene moieties were synthesized in good total yield by the McMurry coupling reaction of dialdehyde **1**. *E,E*-**12T10A** was converted to cyclo[12](3,4-dibutyl-2,5-thienylene-ethynylene) **12T12A** in 20% yield by bromination-dehydrobromination procedure. Furthermore, the synthesis of **12T12A** was carried out by using double elimination procedure starting from the sulfone dianion $\mathbf{2}^{2-}$ and dialdehyde **1**. The crystal structure of *E,E*-**12T10A** was determined by X-ray analysis. In the solid state, macrocyclic oligothiophenes formed nanostructured polymorphs such as single crystals, petal-shaped structure, and chained lumps depending on the ring size.

INTRODUCTION

Recently, redox-active nanorings have attracted considerable attention for their single-molecule electronics, nano-fabrication, and unusual electronic and optical properties.[1,2] Among them, giant macrocycles composed of thienylene, ethynylene, and vinylene building blocks are regarded as an infinite π-conjugated system with a large inner cavity, and hence their physical properties are strongly affected by their structures in solution and the solid state.[3] Macrocyclic thiophenes have both moderate molecular rigidity and flexibility,[4,5] and the nanophase separation between interior and exterior sites in large

macrocycles results in the formation of attractive one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) supramolecular nanostructures.[6,7] We previously reported the syntheses and valuable photophysical properties of macrocyclic oligothiophenes *E,E*-**12T10A**, *E,E,E*-**18T15A**, and *E,E,E,E*-**24T20A**,[8] as well as cyclo[12](3,4-dibutyl-2,5-thienylene-ethynylene) **12T12A**.[9] In this paper, we report an alternative synthesis of **12T12A** using 'bromination–dehydrobromination procedure' together with the formation of nanostructured polymorphs from *E,E*-**12T10A**, *E,E,E*-**18T15A**, and *E,E,E,E*-**24T20A**.

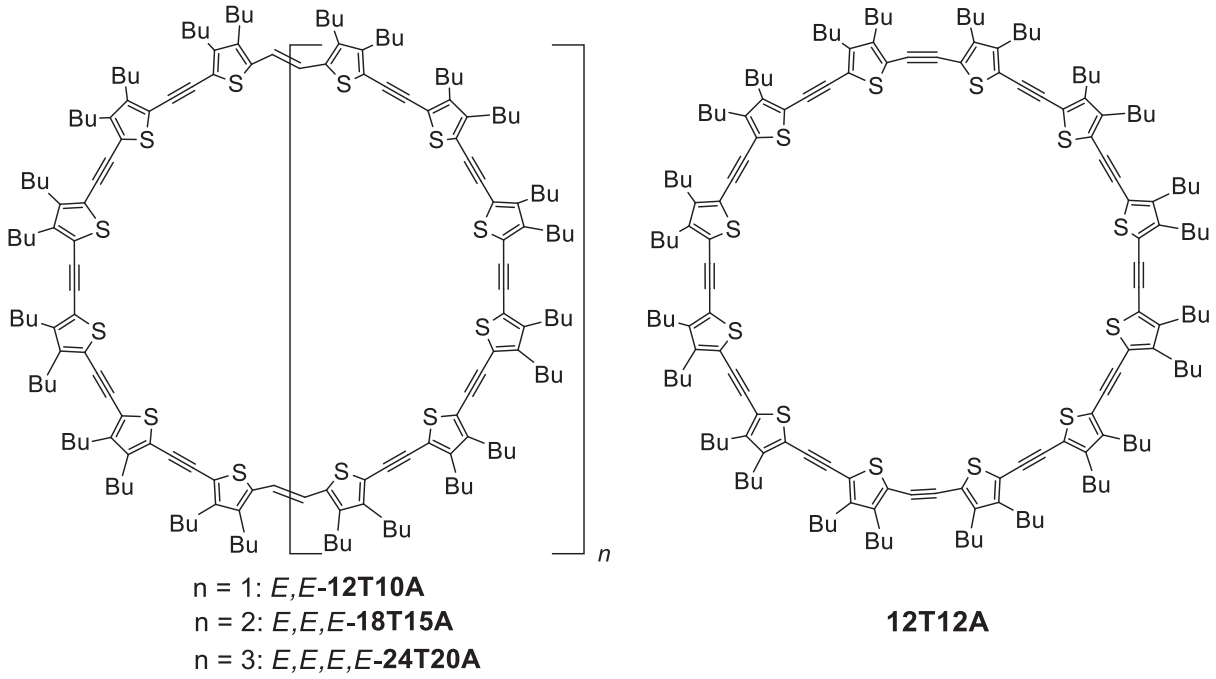
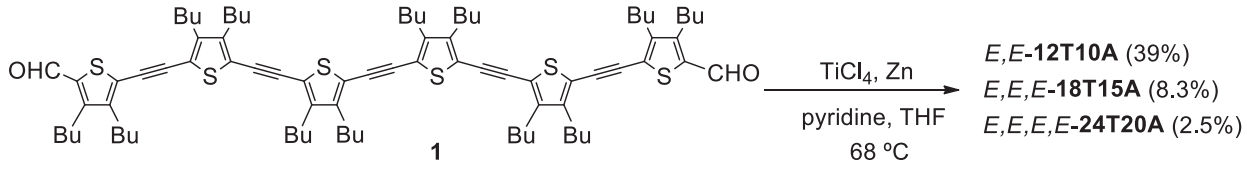


Figure 1. Chemical formulae of *E,E*-**12T10A**, *E,E,E*-**18T15A**, *E,E,E,E*-**24T20A**, and **12T12A**

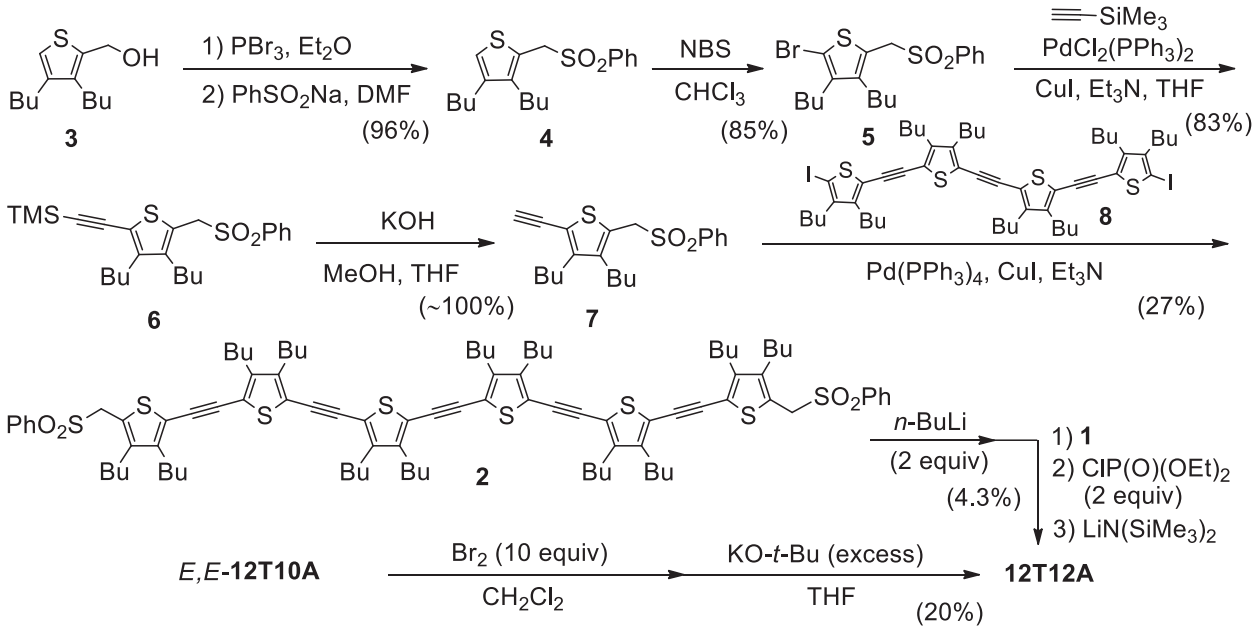
RESULTS AND DISCUSSION

The synthesis of *E,E*-**12T10A**, *E,E,E*-**18T15A**, and *E,E,E,E*-**24T20A** was performed by using a McMurry coupling of the dialdehyde **1** with low-valent titanium reagent (Scheme 1).[8] *E,E*-**12T10A** was obtained in 39% yield as a main product, together with *E,E,E*-**18T15A** (8.3%) and *E,E,E,E*-**24T20A** (2.5%).[10] *E,E*-**12T10A**, *E,E,E*-**18T15A**, and *E,E,E,E*-**24T20A** are stable in the solid state in air at room temperature in spite of the fairly low oxidation potentials ($E^1_{1/2}$ = 0.31–0.33 V; $E^2_{1/2}$ = 0.50–0.52 V *vs* Fc/Fc^+ in dichloromethane).[11]



Scheme 1. Synthesis of *E,E*-**12T10A**, *E,E,E*-**18T15A**, and *E,E,E,E*-**24T20A**

The synthesis of **12T12A** was carried out by the two synthetic routes (Scheme 2). First, we performed 'double elimination procedure'.[12] The sulfone dianion prepared from **2** was reacted with the dialdehyde **1** (1 equiv), and the adduct was reacted with diethyl chlorophosphate (2 equiv), followed by treatment with lithium hexamethyldisilazide (4 equiv) producing **12T12A** in 4.3% overall yield. Second, we employed 'bromination–dehydrobromination procedure' similar to the synthesis of **10T10A**.[13] Bromination of *E,E*-**12T10A**, followed by dehydrobromination with potassium *t*-butoxide, produced **12T12A** in 20% overall yield. Although the bromination–dehydrobromination procedure is sensitive to the amounts of both bromine and potassium *t*-butoxide, a considerable quantity of **12T12A** can be prepared using this procedure.



Scheme 2. Synthesis of **12T12A** by double elimination route and bromination–dehydrobromination procedure

Macrocyclic oligothiophenes *E,E*-**12T10A**, *E,E,E*-**18T15A**, and *E,E,E,E*-**24T20A** form different supramolecular structures in the solid state owing to the nanophase separation based on their interior and exterior sites, exhibiting a ring-size dependence of the morphology. Although macrocyclic oligothiophenes *E,E*-**12T10A**, *E,E,E*-**18T15A**, and *E,E,E,E*-**24T20A** consist of exactly the same unit $(C_{84}H_{110}S_6)_n$, *E,E*-**12T10A** forms crystals on recrystallization from chloroform–decane (Figure 2a), *E,E,E*-**18T15A** forms a petal structure from chloroform–acetone (Figure 2b), and *E,E,E,E*-**24T20A** forms chained lumps from chloroform–ethyl acetate (Figure 2c).[14] None of these polymorphs contains any solvent determined by ^{1}H NMR measurements, and the morphological difference depends on the ring size and conformation.

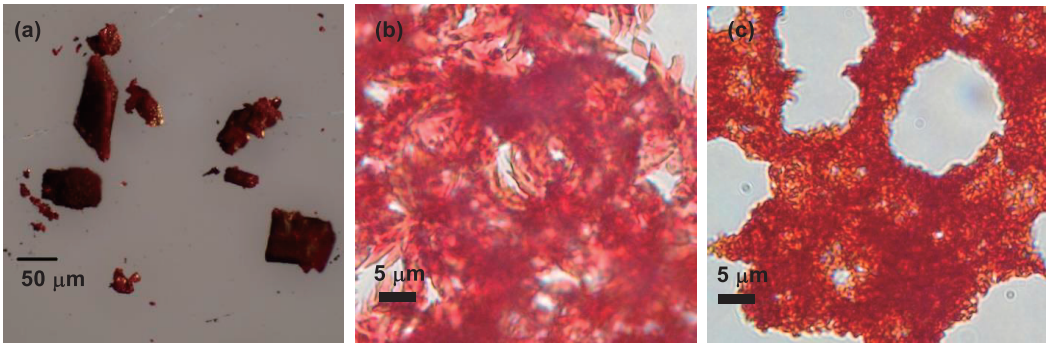


Figure 2. Optical images of (a) crystals of *E,E*-**12T10A**, (b) petals of *E,E,E*-**18T15A**, and (c) chained lumps of *E,E,E,E*-**24T20A**

As shown in Figure 2a, a single crystal of *E,E*-**12T10A** was prepared from chloroform-decane and employed for X-ray analysis (Figure 3). In our previous work,[13] the macrocycle *E,E*-**10T8A** composed of ten thienylene units exhibited a round shape with all thienylene units in *cisoid* structure, and heptane molecules were incorporated in the inner cavity. In the case of *E,E*-**12T10A**, however, two thienylene units are in *transoid* structure to occupy the center of the macrocycle (Figure 3a). There was a disorder in the position of vinylene moieties, which is a reason for the relatively large R_1 value (0.093). The resultant small cavity is filled with butyl groups of neighboring molecules. As a consequence, the single crystal involves no solvent molecule. *E,E*-**12T10A** has a slightly bent chair-like structure (Figure 3b). In the molecular packing, molecules stack along the *a*-axis, and there is almost no significant intermolecular π-π interaction between the thiophenes of *E,E*-**12T10A** (Figure 3c).

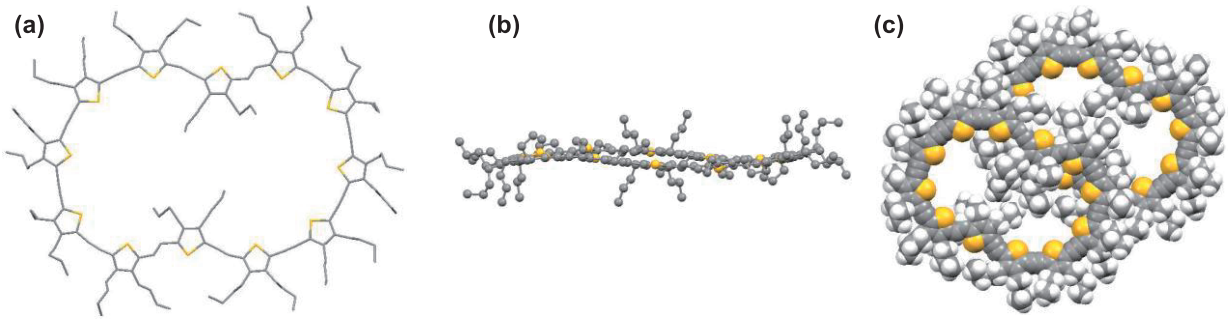


Figure 3. X-Ray structure of *E,E*-**12T10A**. (a) Top view, (b) side view, and (c) packing structure. Hydrogen atoms omitted for clarity except for (c)

In summary, π-expanded macrocyclic oligothiophenes *E,E*-**12T10A**, *E,E,E*-**18T15A**, and *E,E,E,E*-**24T20A** were synthesized by McMurry coupling. On the other hand, **12T12A** was synthesized either by double elimination procedure of the adduct prepared from the sulfone dianion and dialdehyde **1** or by bromination–dehydrobromination procedure. In the solid state, macrocycles afforded nanostructured polymorphs depending on the ring size and conformation. *E,E*-**12T10A** forms crystals,

E,E,E-**18T15A** forms a petal structure, and *E,E,E,E*-**24T20A** forms chained lumps. Furthermore, the crystal structure of *E,E*-**12T10A** was determined by X-ray analysis.

EXPERIMENTAL

McMurry coupling reaction of the dialdehyde (1). To a solution of $TiCl_4$ (21 mmol, 4.02 g) in THF (200 mL) was added zinc powder (42 mmol, 2.72 g) at room temperature, and the suspension was refluxed with stirring for 2 h. Then a solution of the dialdehyde **1**[8] (2.0 mmol, 2.69 g) and pyridine (31 mmol, 2.45 g) in THF (200 mL) was added dropwise to the above gently refluxing suspension for 5 h at 68 ºC. After refluxing for 15 h, the reaction mixture was cooled to room temperature. A solution of 10% aqueous K_2CO_3 (100 mL) was carefully introduced with stirring, and then $CHCl_3$ (100 mL) was added. After stirring for 30 min, the mixture was washed with aqueous NH_4Cl and the aqueous layer was extracted with $CHCl_3$. The combined organic phase was dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was chromatographed on deactivated silica gel (activity V) using a mixture of hexane and CH_2Cl_2 (3:1, v/v) as the eluent. First, the cyclic dimer *E,E*-**12T10A** (473 mg) was separated by recrystallization from hexane–$CHCl_3$. Then the filtrate was concentrated and the residue was further purified by GPC to afford a mixture of the dimeric products (*E,E* : *E,Z* : *Z,Z* = 25 : 1 : 2) (610 mg), the cyclic trimer *E,E,E*-**18T15A** (219 mg), and the cyclic tetramer *E,E,E,E*-**24T20A** (66 mg). From the mixture of *E,E*-, *E,Z*-, and *Z,Z*-isomers of **12T10A**, *E,E*-**12T10A** was separated by recrystallization from hexane–$CHCl_3$ to give pure *E,E*-**12T10A** (552 mg).

E,E-**12T10A**: red crystals (39%), ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.96 (s, 4H), 2.69–2.60 (m, 48H), 1.64–1.39 (m, 96H), 0.99–0.95 (m, 72H); ^{13}C NMR ($CDCl_3$, 125MHz), δ 148.35, 145.54, 145.36, 145.26, 140.34, 138.17, 120.34, 120.18, 120.15, 120.04, 119.96, 119.73, 116.53, 90.56, 90.51, 89.99, 89.96, 89.79, 33.29, 32.57 (5C), 28.63, 28.52, 27.19, 22.86 (8C), 22.77, 14.07, 14.04 (2C), 14.02 (2C), 14.00; LDI–TOF–MS *m/z* 2622 (M^+); UV–vis. (CH_2Cl_2) λ_{max} (ε) 452 (295,000). Anal. Calcd for $C_{168}H_{220}S_{12}$: C, 76.89%; H, 8.45%. Found: C, 76.86%, H, 8.25%.

E,E,E-**18T15A**: red powder (8.3%), ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.98 (s, 6H), 2.70–2.59 (m, 72H), 1.63–1.39 (m, 144H), 0.99–0.95 (m, 108H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.25, 146.26, 146.16, 146.11, 145.86, 140.57, 138.20, 120.11, 119.81 (2C), 119.70, 119.37, 116.25, 90.30, 89.86, 89.62, 89.53, 89.43, 33.40, 32.56 (2C), 32.52 (3C), 32.46, 28.57 (2C), 28.48, 28.42, 26.96, 22.80 (4C), 22.76 (2C), 14.01 (4C), 13.94 (2C); MALDI–TOF–MS *m/z* 3936 (M^+); UV–vis. (CH_2Cl_2) λ_{max} (ε) 473 (418,000). Anal. Calcd for $C_{252}H_{330}S_{18}$: C, 76.89%; H, 8.45%. Found: C, 76.69%; H, 8.05%.

E,E,E,E-**24T20A**: red powder (2.5%), ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.98 (s, 8H), 2.70–2.59 (m, 96H), 1.63–1.39 (m, 192H), 1.00–0.95 (m, 144H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.23, 146.46, 146.41, 146.34, 146.04, 140.60, 138.21, 120.01, 119.77, 119.70, 119.59, 119.30, 116.22, 90.25, 89.86, 89.58,

89.48, 89.40, 33.45, 32.58, 32.49 (6C), 28.51 (4C), 28.43, 26.94, 22.80 (4C), 22.76, 14.02 (4C), 13.97; MALDI–TOF–MS *m/z* 5249 (M^+); UV–vis. (CH_2Cl_2) λ_{max} (ε) 478 (528,000). Anal. Calcd for $C_{336}H_{440}S_{24}$: C, 76.89%; H, 8.45%. Found: C, 76.70%; H, 8.35%.

2-Benzenesulfonylmethyl-3,4-dibutylthiophene (4). To a solution of **3** (9.79 g, 43.2 mmol) in Et_2O (100 mL) was slowly added PBr_3 (4.1 mL, 44 mmol) under nitrogen, and the mixture was stirred overnight at room temperature. To the reaction mixture was added saturated aq. $NaHCO_3$ solution and extracted with Et_2O. The organic phase was washed with saturated aq. $NaHCO_3$ solution and then brine, and dried over $MgSO_4$. After filtration, the solvent was removed in *vacuo*. Since the bromide was unstable under air, the bromide was used for next reaction without further purification.

To a solution of the bromide in DMF (100 mL) was slowly added $PhSO_2Na$ (9.73 g, 59.3 mmol) under nitrogen, and the mixture was stirred for 90 min at 120 °C. The reaction mixture was cooled to room temperature, and water (150 mL) was added. The reaction mixture was extracted with $CHCl_3$, and the organic phase was washed with 2M hydrochloric acid and dried over $MgSO_4$. After filtration, the solvent was removed in *vacuo*. The residue was chromatographed on deactivated silica gel (act. V) column using benzene as eluent to afford 14.5 g (96%) of **4** as brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.70 (2H, d, J = 7.3 Hz), 7.62 (1H, t, J = 7.7 Hz), 7.47 (2H, t, J = 8.2 Hz), 6.87 (1H, s), 4.47 (2H, s), 2.43 (2H, t, J = 3.8 Hz), 2.40 (2H, t, J = 4.0 Hz), 2.16 (2H, t, J = 8.0 Hz), 1.53 (2H, q, J = 5.2 Hz), 1.35 (2H, q, J = 7.4 Hz), 1.27–1.19 (4H, m), 0.94 (3H, t, J = 7.5 Hz), 0.86 (3H, t, J = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 142.34, 141.49, 137.29, 133.23, 128.36, 128.07, 127.70, 122.03, 120.83, 55.80, 31.84, 31.44, 28.26, 25.76, 22.41, 22.09, 13.65, 13.52; MS (EI) *m/z* 350 (M^+). Anal. Calcd for $C_{19}H_{26}O_2S_2$: C, 65.10%; H, 7.48%. Found: C, 65.01%; H, 7.39%.

2-Benzenesulfonylmethyl-5-bromo-3,4-dibutylthiophene (5). To a solution of **4** (14.4 g, 41.1 mmol) in $CHCl_3$ (175 mL) and acetic acid (25 mL) was slowly added NBS (10.2 g, 57.4 mmol), and the reaction mixture was stirred for 3 h at room temperature. Saturated aq. $NaHCO_3$ solution was added, and the mixture was extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$. After filtration, the solvent was removed in *vacuo*. The residue was chromatographed on deactivated silica gel (act. V) column using benzene as eluent to afford 15.0 g (85%) of **5** as brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.73 (2H, d, J = 7.0 Hz), 7.64 (1H, t, J = 7.5 Hz), 7.49 (2H, t, J = 8.0 Hz), 4.39 (2H, s), 2.43 (2H, t, J = 7.6 Hz), 2.10 (2H, t, J = 8.1 Hz), 1.39–1.15 (8H, m), 0.95–0.92 (3H, m), 0.87–0.84 (3H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 142.86, 141.02, 137.29, 133.78, 128.81, 128.38, 122.57, 110.58, 55.68, 32.22, 31.37, 27.82, 26.46, 22.42, 22.29, 13.68, 13.53. Anal. Calcd for $C_{19}H_{25}BrO_2S_2$: C, 53.14%; H, 5.87%. Found: C, 53.31%; H, 5.89%.

2-Benzenesulfonylmethyl-3,4-dibutyl-5-trimethylsilylethynylthiophene (6). To a mixture of **5** (15.0 g, 34.9 mmol), $PdCl_2(PPh_3)_2$ (0.96 g, 3.9 mol%), CuI (0.51 g, 7.7 mol%), and trimethylsilylacetylene (6.0 mL, 43 mmol) in THF (50 mL) was added Et_3N (20 mL) under nitrogen, and the mixture was stirred overnight at 70 °C. The reaction mixture was cooled to room temperature. To the reaction mixture was added saturated aq. NH_4Cl solution. The mixture was extracted with CH_2Cl_2 and dried over $MgSO_4$. After filtration, the solvent was removed in *vacuo*. The residue was passed through a short column of deactivated Al_2O_3 (act. V) and chromatographed on deactivated silica gel (act. V) column using benzene as eluent to afford 12.9 g (83%) of **6** as light brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.72 (2H, d, J = 7.6 Hz), 7.70–7.61 (1H, m), 7.49–7.45 (2H, m), 4.42 (2H, s), 2.52 (2H, t, J = 7.8 Hz), 2.05 (2H, t, J = 7.9 Hz), 1.46–1.14 (8H, m), 0.93 (3H, t, J = 7.3 Hz), 0.84 (3H, t, J = 7.2 Hz), 0.26–0.21 (9H, m).

2-Benzenesulfonylmethyl-3,4-dibutyl-5-ethynylthiophene (7). To a solution of **6** (1.99 g, 4.45 mmol) in MeOH (50 mL) and THF (10 mL) was added aq. 2M KOH solution (5 mL), and the mixture was stirred for 1 h. Benzene was added to the reaction mixture, and the solvent was evaporated in *vacuo*. The organic phase was washed with aq. NH_4Cl solution and dried over $MgSO_4$. After filtration, the solvent was removed in *vacuo*. The residue was passed through a short column of deactivated silica gel (act. V) using benzene as the eluent to afford 1.67 g of **7** in quantitative yield as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.73 (2H, t, J = 8.7 Hz), 7.63 (1H, t, J = 8.7 Hz), 7.51–7.46 (2H, m), 4.43 (1H, s), 4.39 (1H, s), 3.44 (1H, s), 2.54 (1H, t, J = 9.6 Hz), 2.42 (1H, t, J = 9.5 Hz), 2.10 (2H, t, J = 8.9 Hz), 1.47–1.15 (8H, m), 0.95–0.84 (6H, m). Since **7** gradually decomposed at room temperature, **7** was used for the follwoing reaction without further purification.

Linear 6T5A-disulfone (2). To a mixture of **7** (1.67 g, 4.45 mmol), **8** (2.24 g, 2.03 mmol), $Pd(PPh_3)_4$ (0.24 g, 10 mol%), and CuI (76.8 mg, 20 mol%) in THF (15 mL) was added Et_3N (5 mL) under nitrogen, and the mixture was stirred overnight. The mixture was filtered through Celite and washed with Et_2O. The organic phase was washed with aq. NH_4Cl solution and dried over $MgSO_4$. After filtration, the solvent was removed in *vacuo*. The residue was chromatographed on deactivated silica gel (act. V) column using benzene as eluent to afford 0.86 g (27%) of **2** as orange solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.75 (4H, d, J = 8.3 Hz), 7.61 (2H, t, J = 7.5 Hz), 7.47 (4H, t, J = 7.8 Hz), 4.46 (4H, s), 2.72–2.68 (10H, m), 2.61 (6H, t, J = 7.5 Hz), 2.14 (4H, t, J = 8.2 Hz), 1.65–1.58 (16H, m), 1.53–1.36 (24H, m), 1.28–1.21 (8H, m), 1.00–0.94 (30H, m), 0.87 (6H, t, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 146.65, 146.40, 146.24, 142.93, 137.57, 133.78, 128.85, 128.52, 128.07, 123.95, 119.54, 119.36, 119.25, 89.33, 89.26, 89.06, 88.94, 56.02, 32.28, 28.28, 28.23, 26.15, 22.56, 22.54, 22.45, 13.82, 13.61. Anal. Calcd for $C_{96}H_{122}O_4S_8$: C, 72.22%; H, 7.70%. Found: C, 72.23%; H, 7.75%.

Synthesis of 12T12A using double elimination procedure. To a solution of **2** (0.658 g, 0.412 mmol) in THF (50 mL) was added *n*-BuLi (0.56 mL, 0.90 mmol) under nitrogen at –78 °C and stirred for 1 h. The mixture was added a solution of **3**[5] (0.646 g, 0.481 mmol) in THF (50 mL) at –78 °C, and stirred for 1 h. To the mixture was added diethyl chlorophosphate (0.15 mL, 1.04 mmol) at –78 °C and the mixture was stirred for 2.5 h. To the mixture was added a solution of LiHMDS (4.50 mmol) in THF (4.5 mL) at –78 °C and the mixture was stirred for 2 h. After warming up to room temperature, the mixture was stirred overnight. To the reaction mixture was added $CHCl_3$, and the organic phase was separated. The organic phase was washed with aq. NH_4Cl solution and dried over $MgSO_4$. After filtration, the solvent was removed in *vacuo*. The residue was passed through a short column of deactivated silica gel (act. V) using $CHCl_3$ as the eluent, and the resulting crude mixture was chromatographed on deactivated silica gel column using hexane/$CHCl_3$ (v/v 3:1) as eluent to afford 46.6 mg (4.3%) of **12T12A** as orange solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.69 (48H, t, J = 7.7 Hz), 1.63–1.57 (48H, m), 1.46–1.39 (48H, m), 0.96 (72H, t, J = 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 145.99, 119.77, 89.60, 32.58, 28.60, 22.84, 14.10; HRMS (MALDI) Calcd. for $C_{168}H_{216}S_{12}$ (M^+) 2617.3551; found, 2617.3399.

Synthesis of 12T12A using bromination–dehydrobromination procedure. To a solution of *E,E*-**12T10A** (82 mg, 0.031 mmol) in CH_2Cl_2 (11 mL) at 0 °C was slowly added a solution [0.30 M] of bromine (1.1 mL, 0.33 mmol) in CH_2Cl_2 *via* syringe under the dark. After stirring for 30 min at 0 °C, sat. aq. $NaHCO_3$ (10 mL) was slowly added to the reaction mixture. The mixture was extracted with CH_2Cl_2, and the organic phase was washed with aq. $Na_2S_2O_3$ and dried over $MgSO_4$. After filtration, the solvent was removed in *vacuo*, and the crude product was used for the next reaction without further purification.

To a solution of the bromide in THF (6 mL) was slowly added a solution [0.24 M] of *tert*-BuOK (5.2 mL, 1.25 mmol) in THF at 0 °C. After stirring for 15 min at 0 °C, the mixture was warm up to room temperature and stirred for 1 h. To the reaction mixture was added sat. aq. NH_4Cl solution (10 mL), and the mixture was extracted with CH_2Cl_2. The organic phase was washed with sat. aq. NH_4Cl solution and dried over $MgSO_4$. After filtration, the solvent was removed in *vacuo* to afford crude product. The same dehydrobromination procedure with *tert*-BuOK (5.2 mL, 1.25 mmol) was repeated again, and the residue was chromatographed on deactivated silica gel column (act. V, hexane/CS_2 (v/v 8:2)) to afford crude **12T12A**. Pure **12T12A** (16.4 mg, 20%) was obtained after recrystallization from benzene.

X-Ray analysis of *E,E*-12T10A. Crystal Data: $C_{168}H_{220}S_{12}$, Mr = 2624.16, triclinic, space group P-1 (No. 14), a = 12.69(10), b = 16.13(8), c = 20.02(9) Å, α = 93.98(3), β = 96.60(15), γ = 107.50(18)°, V = 3859(39) Å^3, Z = 1, ρ_{calcd} = 1.129 g cm^{-3}; Mo Kα radiation (graphite monochromator, λ = 0.71070 Å), μ = 2.19 cm^{-1}, T = –180 °C. 13309 data (Rint = 0.0581, $2\theta < 50°$), were collected on a Rigaku/MSC Saturn CCD diffractometer. The structure was solved by direct methods (SHELXS-97) and refined by

full-matrix least-squares against $F2$. All the non-hydrogen atoms in the molecule *E,E*-**12T10A** were refined anisotropically. The hydogen atoms in *E,E*-**12T10A** were placed at the calculated positions and not refined. There was disorder in positions between ethylene and one of acetylene parts, which were also refined anisotropically. $R_1 = 0.093$, $wR_2 = 0.218$ for 13309 independent observed reflections ($I > 2.00\ \sigma(I)$, $2\ \theta < 50°$) with 852 variable, GOF = 1.291.

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10. Small amounts of *E,E,E,E,E*-**30T25A** (1.2%) and *E,E,E,E,E,* *E*-**36T30A** (0.2%) were also obtained in this reaction.
11. HOMO levels of *E,E*-**12T10A**, *E,E,E*-**18T15A**, and *E,E,E,E*-**24T20A** calculated at RB3LYP/6-31G(d,p) level are in good agreement with the low oxidation potentials measured by cyclic voltammetry.
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14. Since macrocyclic oligothiophenes are not sufficiently soluble in the common organic solvents, chloroform was used for dissolving *E,E*-**12T10A**, *E,E,E*-**18T15A**, and *E,E,E,E*-**24T20A**. Semishape-persistent *E,E*-**12T10A** and *E,E,E*-**18T15A** formed single crystals and petal-structure, respectively. However, coformationally mobile *E,E,E,E*-**24T20A** formed chained lumps owing to less structural regularity in the solid state.