\[\text{π-EXPANDED CYCLIC OLIGOTHIOPHENE 12-MERS AS SEMISHAPE-PERSISTENT MACROCYCLES}\]

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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 \(2^-\) 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. 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. Macroyclic thiophenes have both moderate molecular rigidity and flexibility, 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.\textsuperscript{6,7} We previously reported the syntheses and valuable photophysical properties of macrocyclic oligothiophenes \textit{E,E}-12\textit{T}10\textit{A}, \textit{E,E,E}-18\textit{T}15\textit{A}, and \textit{E,E,E,E}-24\textit{T}20\textit{A},\textsuperscript{8} as well as cyclo[12]([3,4-dibutyl-2,5-thienylene-ethynylene]) 12\textit{T}12\textit{A}.\textsuperscript{9} In this paper, we report an alternative synthesis of 12\textit{T}12\textit{A} using ‘bromination‒dehydrobromination procedure’ together with the formation of nanostructured polymorphs from \textit{E,E}-12\textit{T}10\textit{A}, \textit{E,E,E}-18\textit{T}15\textit{A}, and \textit{E,E,E,E}-24\textit{T}20\textit{A}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Chemical formulae of \textit{E,E}-12\textit{T}10\textit{A}, \textit{E,E,E}-18\textit{T}15\textit{A}, \textit{E,E,E,E}-24\textit{T}20\textit{A}, and 12\textit{T}12\textit{A}.}
\end{figure}

\section*{RESULTS AND DISCUSSION}

The synthesis of \textit{E,E}-12\textit{T}10\textit{A}, \textit{E,E,E}-18\textit{T}15\textit{A}, and \textit{E,E,E,E}-24\textit{T}20\textit{A} was performed by using a McMurry coupling of the dialdehyde 1 with low-valent titanium reagent (Scheme 1).\textsuperscript{8} \textit{E,E}-12\textit{T}10\textit{A} was obtained in 39\% yield as a main product, together with \textit{E,E,E}-18\textit{T}15\textit{A} (8.3\%) and \textit{E,E,E,E}-24\textit{T}20\textit{A} (2.5\%).\textsuperscript{10} \textit{E,E}-12\textit{T}10\textit{A}, \textit{E,E,E}-18\textit{T}15\textit{A}, and \textit{E,E,E,E}-24\textit{T}20\textit{A} are stable in the solid state in air at room temperature in spite of the fairly low oxidation potentials (E\textsubscript{1/2} = 0.31–0.33 V; E\textsubscript{2/1} = 0.50–0.52 V vs Fe/Fc\textsuperscript{+} in dichloromethane).\textsuperscript{11}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{scheme1.png}
\caption{Synthesis of \textit{E,E}-12\textit{T}10\textit{A}, \textit{E,E,E}-18\textit{T}15\textit{A}, and \textit{E,E,E,E}-24\textit{T}20\textit{A}.}
\end{figure}

\begin{equation}
\begin{array}{c}
\text{OHC} \equiv \text{Bu} \equiv \text{S} \equiv \text{Bu} \equiv \text{S} \equiv \text{Bu} \equiv \text{S} \equiv \text{Bu} \equiv \text{S} \equiv \text{Bu} \equiv \text{S} \equiv \text{Bu} \equiv \text{S} \equiv \text{Bu} \equiv \text{S} \equiv \text{Bu} \equiv \text{CHO} \equiv \text{TiCl}_{4}, \text{Zn, pyridine, THF, 68 °C} \\
\end{array}
\end{equation}

\begin{equation}
\begin{array}{c}
\text{E,E}-12\text{T}10\text{A} (39\%) \\
\text{E,E,E}-18\text{T}15\text{A} (8.3\%) \\
\text{E,E,E,E}-24\text{T}20\text{A} (2.5\%)
\end{array}
\end{equation}
The synthesis of 12T12A was carried out by the two synthetic routes (Scheme 2). First, we performed ‘double elimination procedure’. 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. 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 \((\text{C}_{84}\text{H}_{110}\text{S}_6)_n\), 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). None of these polymorphs contains any solvent determined by \(^1\text{H}\) 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 \(\pi-\pi\) 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, \(\pi\)-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 °C. After refluxing for 15 h, the reaction mixture was cooled to room temperature. A solution of 10% aqueous K$_2$CO$_3$ (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$_4$Cl 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$_2$Cl$_2$ (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) $\delta$ 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), $\delta$ 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$_2$Cl$_2$) $\lambda_{max}$ (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%.

$E,E$-$18T15A$: red powder (8.3%), $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 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) $\delta$ 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$_2$Cl$_2$) $\lambda_{max}$ (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%.

$E,E,E$-$24T20A$: red powder (2.5%), $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 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) $\delta$ 148.23, 146.46, 146.41, 146.34, 146.04, 138.21, 120.01, 119.77, 119.70, 119.59, 119.30, 116.22, 90.25, 89.86, 89.58,
MALDI–TOF–MS \(m/z\) 5249 (M⁺); UV–vis. (CH₂Cl₂) \(\lambda_{\text{max}}(\varepsilon)\) 478 (528,000). Anal. Calcd for C₃₃6H₄₄0S₂₄: C, 76.89%; H, 8.45%. Found: C, 76.70%; H, 8.35%.

2-Benzensulfonylmethyl-3,4-dibutylthiophene (4). To a solution of 3 (9.79 g, 43.2 mmol) in Et₂O (100 mL) was slowly added PBr₃ (4.1 mL, 44 mmol) under nitrogen, and the mixture was stirred overnight at room temperature. To the reaction mixture was added saturated aq. NaHCO₃ solution and extracted with Et₂O. The organic phase was washed with saturated aq. NaHCO₃ solution and then brine, and dried over MgSO₄. 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 PhSO₂Na (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 CHCl₃, and the organic phase was washed with 2M hydrochloric acid and dried over MgSO₄. 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. ¹H NMR (500 MHz, CDCl₃): \(\delta\) (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); ¹³C NMR (125 MHz, CDCl₃): \(\delta\) (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 C₁₉H₂₆O₂S₂: C, 65.10%; H, 7.48%. Found: C, 65.01%; H, 7.39%.

2-Benzensulfonylmethyl-5-bromo-3,4-dibutylthiophene (5). To a solution of 4 (14.4 g, 41.1 mmol) in CHCl₃ (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. NaHCO₃ solution was added, and the mixture was extracted with CHCl₃, and the reaction mixture was extracted with CHCl₃, and the organic phase was washed with CHCl₃, and the organic phase was washed with 2M hydrochloric acid and dried over MgSO₄. 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. ¹H NMR (500 MHz, CDCl₃): \(\delta\) (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); ¹³C NMR (125 MHz, CDCl₃): \(\delta\) (ppm) 142.86, 141.49, 137.29, 133.32, 128.81, 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 C₁₉H₂₅BrO₂S₂: C, 53.14%; H, 5.87%. Found: C, 53.31%; H, 5.89%.
2-Benzensulfonylmethyl-3,4-dibutyl-5-trimethylsilylethynylthiophene (6). To a mixture of 5 (15.0 g, 34.9 mmol), PdCl₂(PPh₃)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 Et₃N (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. NH₄Cl solution. The mixture was extracted with CH₂Cl₂ and dried over MgSO₄. After filtration, the solvent was removed in vacuo. The residue was passed through a short column of deactivated Al₂O₃ (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. ¹H NMR (500 MHz, CDCl₃): 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-Benzensulfonylmethyl-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. NH₄Cl solution and dried over MgSO₄. 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. ¹H NMR (500 MHz, CDCl₃): 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 following 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(PPh₃)₄ (0.24 g, 10 mol%), and CuI (76.8 mg, 20 mol%) in THF (15 mL) was added Et₃N (5 mL) under nitrogen, and the mixture was stirred overnight. The mixture was filtered through Celite and washed with Et₂O. The organic phase was washed with aq. NH₄Cl solution and dried over MgSO₄. 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. ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (125 MHz, CDCl₃): 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 C₉₆H₁₂₂O₄S₈: 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 (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 LiHMD S (4.50 mmol) in THF (4.5 mL) at −78 °C and 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. 1H 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); 13C 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 C168H216S12 (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 12T12A. 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, ρcalc. = 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, 2θ < 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 $F_2$. All the non-hydrogen atoms in the molecule $E,E$-$12T10A$ were refined anisotropically. The hydrogen 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 ($I > 2.00 \sigma(I)$, $2 \theta < 50^\circ$) with 852 variable, GOF = 1.291.

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**REFERENCES AND NOTES**


10. Small amounts of *E,E,E,E,E-30T25A* (1.2%) and *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.


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.