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Oligo(octithienylene-diethynylene)s as Unprecedentedly Long Conjugated Nanomolecules

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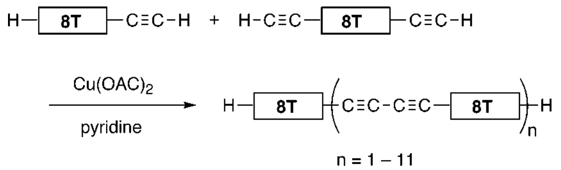
ABSTRACT



8T: tetraoctyloctithiophene

A series of oligo(octithienylene-diethynylene)s alternately composed of octithiophene and diacetylene units have been prepared by a random Eglinton coupling reaction among mono- and diethynyloctithiophenes. The largest compound isolated in the oligomeric series is comprised of twelve octithiophene units and eleven diacetylene units, and its molecular length reaches ca. 43 nm, which is the longest among single-component conjugated nanomolecules.

Structurally well-defined conjugated nanoscale molecules have currently attracted much attention in terms of molecular electronic materials that are finding various applications to electrical conductors, photovoltaic cells, electroluminescent devices, nonlinear optics, and field effect transistors.[1] In addition, the rod type of single-component molecules are expected to serve as promising molecular wires that will be indispensable to forthcoming single-molecular electronic devices.[2] Recent improved synthetic techniques allowed the appearance of very long molecules, as exemplified by the meso-meso-linked zinc(II) porphyrin 128-oligomer reaching even ca. 100 nm in length.[3] However, it is still problematic to obtain fully conjugated π-molecules suitable for nanoarchitecture, which must meet many requirements: ready accessibility, controlled lengths, versatile structural modification, and high tractability. There have been so far a still limited number of such molecules with lengths of more than 10 nm.[4] We report here new, extraordinarily long conjugated molecules, oligo(octithienylene-diethynylene)s **1a−k**. These compounds, comprised of alternating octithiophene and diacetylene units, have a sequence of molecular lengths increasing at a regular interval of 3.6 nm from 6.6 nm up to 42.9 nm and accordingly have a possibility for use as a molecular kit for nanoarchitecture.

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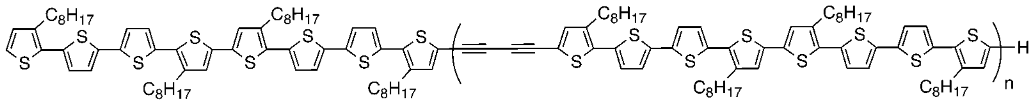

1a: n = 1; **1b**: n = 2;**1c**: n= 3;**1d**: n = 4;**1e**: n = 5;**1f**: n = 6;
1g: n = 7; **1h**: n = 8; **1i**: n = 9; **1j**: n =10; **1k**: n = 11

The synthesis of oligo(octithienylene-diethynylene)s **1a**−**k** was accomplished according to Scheme 1. The key oligomerization reaction utilizes a random oxidative coupling of mono- and diethynyl derivatives, which very effectively proceeds to form high-coupling products. Although the yield of each product is considerably low due to wide product dispersion, this approach has the great advantage of the favorite one-pot availability of all sequential homologues. Diederich's group previously utilized this protocol for the synthesis of a series of poly(triacetylene) rods with lengths up to 17.8 nm.[4f,g,5] Our group also adopted the same approach for the synthesis of a series of long oligothiophenes up to the 48-mer with an 18.6 nm length.[4h] An issue of this approach is how to isolate the sequential products, which is conveniently carried out using their size differences. In the present experiment, we intended to take advantage of large differences in molecular size due to repeated intervals of the tetraoctyloctithiophene-diacetylene segment. First, dioctylquaterthiophene **4T**, obtained in 85% yield by the Ni(II)-catalyzed cross coupling (Kumada coupling) of the dibromobithiophene **2** with a Grignard reagent of 2-bromo-3-octylthiophene **3**,[6] was dimerized in 31% yield to tetraoctyloctithiophene **8T** by deprotonation with butyllithium, followed by $CuCl_2$ oxidation. Then, the treatment of **8T** with 1.4 molar equiv of *N*-bromosuccimide (NBS) led to the formation of a mixture of the mono- and dibromo derivatives **4** and **5**, which, without isolation, were subsequently reacted with trimethylsilylacetylene in the presence of catalytic Pd(PPh_3)$_4$ to give a mixture of the trimethylsilylethynyl derivatives **6** and **7** and then desilylated with potassium hydroxide to the ethynyl derivatives **8** and **9**. An Eglinton coupling reaction using the mixture with copper(II) acetate in pyridine gave a series of the oligo(octithienylene-diethynylene)s **1a**−**k**, which were successfully separated into the individual homologues by preparative gel-permeation (size exclusion) liquid chromatography.[7,8] The largest compound **1k** isolated in this oligomeric series is composed of twelve octithiophene units and eleven diacetylene units. Although higher homologues were appreciably detected, their isolation was unsuccessful due to insufficient size differences.

All the obtained oligo(octithienylene-diethynylene)s are dark-red viscous oils. The lower homologues are considerably soluble in common solvents, but the higher homologues reduce their solubilities with the chain extension. Their structures were characterized by NMR and mass spectroscopic analyses as well as analytical GPLC measurements. All the compounds showed appropriate ^{1}H NMR spectra with multiple signals assignable to the thienyl protons in the range of δ 6.9−7.2 as well as to the octyl protons at δ 0.88 (CH_3), 1.28 (CH_2), 1.67 (CH_2), and 2.77 ($ArCH_2$). However, since the close homologues gave very similar spectra, the NMR spectra were not necessarily decisive for their structural determination. On the other hand, the MALDI-TOF mass spectra were very effective because of the indication of

Scheme 1

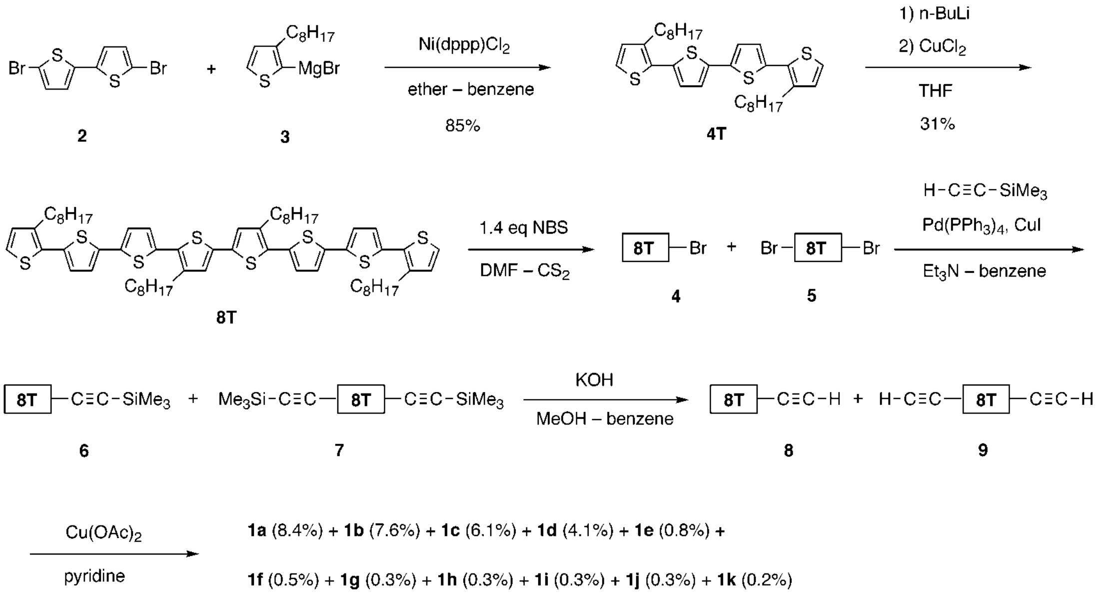

Table 1. Spectral Data of Oligo(octithienylene-diethynylene)s **1**

compd	MS $M^+/m/z$ (calcd)[a]	GPLC MW[b]	λ_{max}/nm (ϵ)[c]
1a	2262.8 (2260.8)	2679	455.5 (140 000)
1b	3415.9 (3414.8)	4188	461.0 (238 000)
1c	4569.3 (4568.9)	6067	463.5 (291 000)
1d	5721.2 (5722.9)	8260	464.0 (409 000)
1e	6876.1 (6876.8)	10 790	465.0 (432 000)
1f	8034.0 (8030.7)	13 520	465.5 (506 000)
1g	9185.3 (9184.6)	17 500	465.5 (626 000)
1h	10 333.1 (10 338.6)	21 580	465.5 (675 000)
1i	11 489.8 (11 492.4)	25 880	465.5 (812 000)
1j	12 644.4 (12 646.4)	29 040	d
1k	13 800.3 (13 800.3)	31 840	d

[a] Mass spectra were measured with a Shimadzu KOMPACT Probe MALDI-TOF instrument using a dithranol matrix. [b] Analytical GPLC molecular weights were determined using a Shodex GPC KF-805 column with polystyrene standards in tetrahydrofuran. [c] Electronic absorption spectra were measured in tetrahydrofuran. [d] Unmeasured due to insolubility.

unambiguous molecular ion peaks, whose data are summarized in Table 1. Figure 1 illustrates the representative mass spectrum of **1k**, which shows only a single peak due to the molecular ion except for low molecular weight peaks due to the used matrix, strongly supporting not only the molecular structure but also the single component.

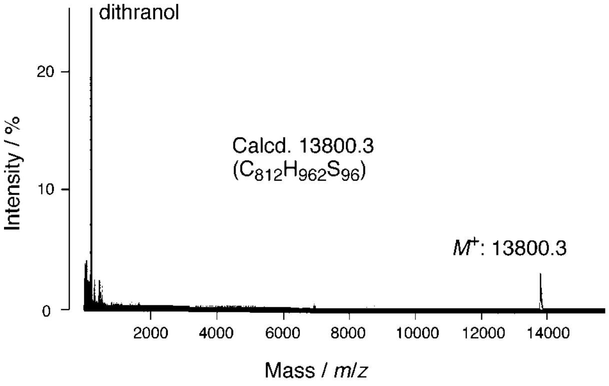

Figure 1. MALDI-TOF mass spectrum of **1k** recorded using a dithranol matrix.

Analytical GPLC measurements also confirmed that these oligo(octithienylene-diethynylene)s **1a**−**k** consist of single components. In addition, it was noticed that the molecular weights of the oligomers measured using polystyrene standards are much larger than the actual values (see Table 1). It was already stated that the molecular weights of rod-type molecules such as oligo(2,5-thienylene-ethynylene)s,[9] oligo(paraphenylene-ethynylene)s,[4a] and oligothiophenes,[4h] when measured by GPLC using randomly shaped polystyrene standards, are much inflated relative to the actual values, while those of coil-type molecules such as oligo(3,4-thienylene-ethynylene)s[10] are much deflated. Figure 2 demonstrates a good continuous relationship of the actual molecular weights vs analytical GPLC molecular weights in the oligomeric series **1**. These results clearly suggest that these oligo(octithienylene-diethynylene)s retain rod-type shapes, even if the molecular chain is elongated. The following molecular sizes are thus estimated on a molecular model with energetically favorable *all-trans* orientation for the oligothiophene segment: **1a**, 6.6 nm; **1b**, 10.2 nm; **1c**, 13.9 nm; **1d**, 17.5 nm; **1e**, 21.1 nm; **1f**, 24.7 nm; **1g**, 28.4

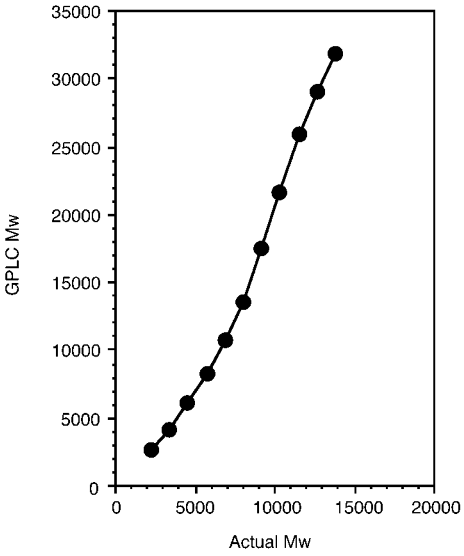

Figure 2. Relationship of molecular weights determined by GPLC in tetrahydrofuran using polystyrene standards versus the actual molecular weights of oligo(octithienylene-diethynylene)s **1**.

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(7) Preparative GPLC was performed on a Japan Analytical Industry (JAI) Recycling Preparative HPLC Model LC-918R with two columns connected in the series JAIGEL 4H and JAIGEL 3H using chloroform as an eluent (3.8 mL/min); the retention volumes were: 209.5 (**1a**), 199.5 (**1b**), 192.0 (**1c**), 186.0 (**1d**), 181.5 (**1e**), 177.5 (**1f**), 174.0 (**1g**), 171.0 (**1h**), 168.5 (**1i**), 165.5 (**1j**), and 164.5 (**1k**) mL.

(8) The yields of oligo(octithienylene-diethynylene)s **1** in Scheme 1 are given as overall yields from tetraoctylocthiophene (**8T**), because the consecutive reactions were carried out without separation of the intermediates **4**−**9**. In a separate experiment, however, the intermediates were isolated in the following yields: **4**, 43%; **5**, 33%; **6**, 92%; **7**, 95%; **8**, 96%; **9**, 91%.

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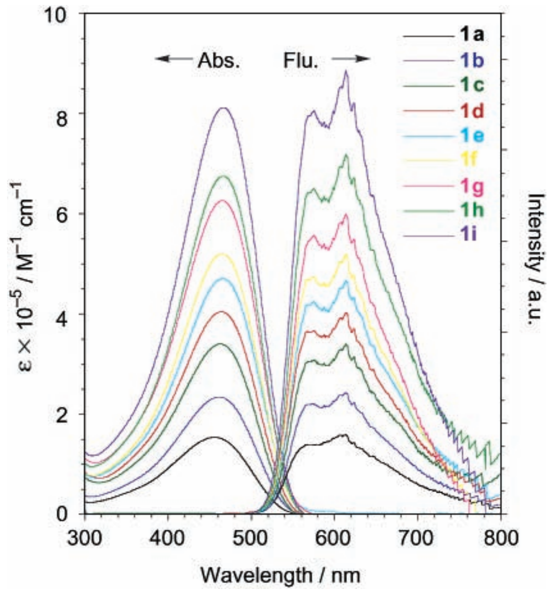

Figure 3. Electronic absorption and fluorescence spectra of oligo(octithienylene-diethynylene)s **1** in tetrahydrofuran.

nm; **1h**, 32.0 nm; **1i**, 35.6 nm; **1j**, 39.3 nm; and **1k**, 42.9 nm. All oligomers except **1a** in this series are beyond 10 nm and thus of the longest class among fully conjugated molecules.

Figure 3 exhibits the electronic absorption and emission spectra of **1**, where the $\pi-\pi^*$ absorption bands are completely unstructured, whereas the emission bands are somewhat structured. The absorption and emission maxima are summarized in Table 1. The absorption band of the first homologue **1a** in the oligomeric series is at a considerably longer wavelength and much more intense ($\lambda_{\max} = 455.5$ nm, $\epsilon = 140\,000$) than the octithiophene **8T** ($\lambda_{\max} = 438.0$ nm, $\epsilon = 57\,300$). The absorption band is progressively red-shifted with increasing chromophore units and converges at the absorption maximum of 465.5 nm for **1f**. This result means that the π-conjugation can spread over a chain segment of about 25 nm. In contrast, the emission bands are insensitive to the chain extension. Although the emission band (Flu$_{\max}$ 576 and 614 nm) of **1a** is considerably red-shifted as compared with that (Flu$_{\max}$ 549 and 588 nm) of **8T**, there are no further red shifts due to the consecutive chain extension.

In summary, the present paper has demonstrated a rapid approach to a series of extraordinarily long nanomolecules. It is suggested that the oligo(ocitithienylene-diethynylene)s thus obtained retain rod-type shapes. Among them, the largest one reaches 40 nm in length, which is long enough for current nanoelectrode spanning. The appearance of such long single-component molecules would greatly promote infant nanochemistry and, furthermore, nanotechnology.

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