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Accounts

Synthesis, Optical, and Conductive Properties of Long Oligothiophenes and Their Utilization as Molecular Wires

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This account reviews the current development of extraordinarily long oligothiophenes involving the 48-mer and 72-mer, which correspond to mono-disperse polymers. The systematic studies of the homologous series have provided valuable information on the optical and conductive properties of α-conjugated thiophene systems: an effective conjugation length extends to around 20 thiophene units in the neutral state and around 30 thiophene units in the oxidation state; this length plays a critical role in determining the electronic structures and conductivities. In addition, the active charge carrier species are both π-dimers and chain dimers, and charge transport occurs through the transfiguration of both species. This account also describes how useful oligothiophenes are as molecular wires allowing photoinduced electron- and/or energy-transfer. The molecular-wire behaviors of sophisticated oligothiophenes that are functionalized with a donor unit and an acceptor unit at the terminal α-positions are demonstrated.

Recently, structurally well-defined conjugated oligomers have attracted much attention as advanced nanoscale molecules.[1] Among them, one of the most extensively studied oligomers is an extended series of α-linked oligothiophenes, which have been intensively regarded not only as good models for conductive polythiophenes but also as essential components of molecular electronics.[2] Non-substituted oligothiophenes, however, become sparingly soluble with the chain extension, and no higher homologues than the 8-mer have been prepared.[3] This inherent disadvantage of oligothiophenes can be overcome by incorporation of solubilizing alkyl groups. Alkyl substitutions at the terminal α-positions allowed an additional extension to a decamer,[4] but are not enough to increase the solubility. On the other hand, alkyl substitutions at the β-positions are very effective, and thus a variety of oligothiophenes with over 10 units have been recently developed: 11-mer,[5] 12-mer,[6,7,8] 15-mer,[7] 16-mer,[8] and 17-mer.[9] The more solubilizing dendron-substituted 17-mers[9,10] and trimethylsilyl-substituted 24-mer[11] were also reported. One may worry about how the introduced substituent groups influence the inherent electronic structures and conductivities of oligothiophenes. However, such alkyl groups, when they are properly arranged so as not to interact with one another, are spread in the lateral direction and not obstructive to molecular stacking for a conduction path.[8,12]

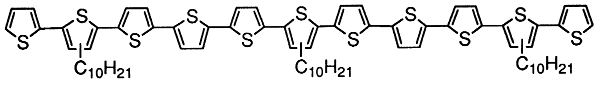
One of the major subjects for studying long oligothiophenes is to understand the relationship between the chain length and the properties of the conjugated system. It is well known that oligothiophenes show a strong π–π^* electron absorption band in the visible region, which is progressively red-shifted with increasing chain length. An early study on the absorption spectra of relatively short oligothiophenes suggested that an effective conjugation length for α-linked polythiophene systems is limited to less than 11 repeat units.[5] Afterwards, it was observed that, even for the longer 15-mer[7] and 16-mer,[8] no complete spectroscopic saturation occurs yet. An extrapolation of the absorption energy/chain length relationship suggested that the effective conjugation length is 20 thiophene units.[13] Even longer oligothiophenes were necessary for more comprehensive understanding. Thus a series of long oligothiophenes with up to 48 thiophene units has been recently studied by our group, and the spectroscopic studies of the homologous series have been very helpful for clarifying the concept of the effective conjugation length regulating the electronic characteristics of polythiophene systems.[14] Furthermore, long oligothiophenes have the advantage of obtaining deep insights into the conduction mechanism of polythiophene systems. The actual species for charge carriers are still controversial. The electronic spectra of long oligothiophenes in the oxidation states have been very useful for the identification of the active carriers.[15]

Another subject for the study of long oligothiophenes is their utilization for the nanoarchitecture of molecular-scale electronic devices, which arouses current interest. Thanks to their ready construction and versatile structural modifications, well-defined oligothiophenes provide promising building blocks as molecular wires. Oligothiophenes with sufficient lengths to span two nanoelectrodes made by lithographic techniques become synthetically available. In this regard, our group very recently has synthesized the longest oligothiophene, 72-mer.[16] In addition, oligothiophenes functionalized with a donor unit and an acceptor unit at the terminal α-positions have a possibility of forming efficient electron- and/or energy-transfer systems. As the first donor/oligothiophene/acceptor triad systems, Effenberger and co-workers recently demonstrated anthryloligothienylporphyrins[17] and anthryloligothienylfullerenes.[18] Although the spacer is still limited to a short oligomer, a nearly quantitative intramolecular energy transfer from the excited donor to the emitting acceptor via the oligomer was observed. Development of such sophisticated electron- and energy-transfer systems is very important for forthcoming molecular-based optoelectronic devices as well as artificial photosynthetic mimics.[19]

Here, we would like to review the latest progress of long oligothiophenes regarding the above topics, which have been mostly investigated by our group. In this article, we use a general and convenient abbreviation **nT** for the nomenclature of oligothiophenes. Since all oligothiophenes described here are modified by alkyl groups, the abbreviation is additionally prefixed with the alkyl group; for example, **Oct-6T** for octyl-substituted sexithiophene.

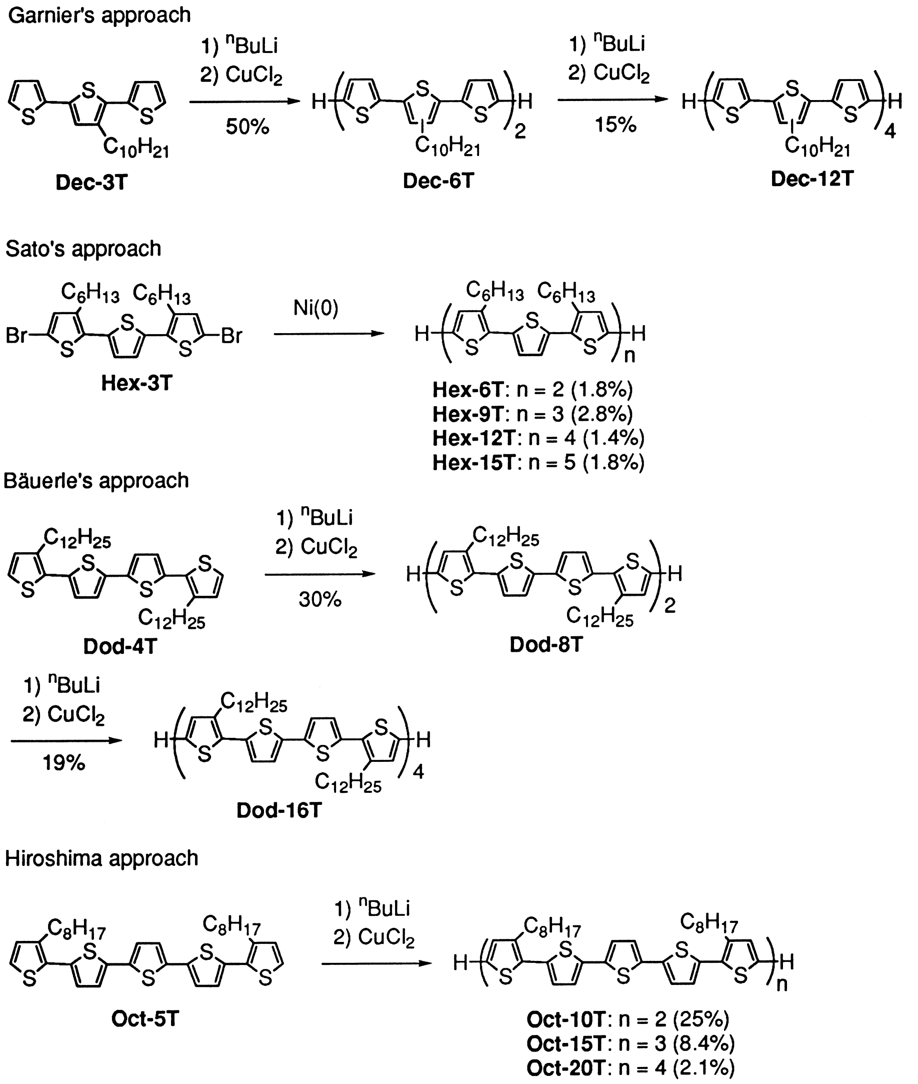
1. Synthesis of Long Oligothiophenes

There are a number of general synthetic methods for short α-oligothiophenes; in particular, modern organometallic aryl–aryl coupling reactions, such as Kumada coupling, Stille coupling, and Suzuki coupling, have been frequently adopted. Although the iteration of these reactions may lead to the formation of long oligomers, one must be troubled with a number of undesired side reactions, such as reduction of organometallic reagents, disproportionation of monofunctional compounds, scrambling via ligand exchange on organometallic complexes,



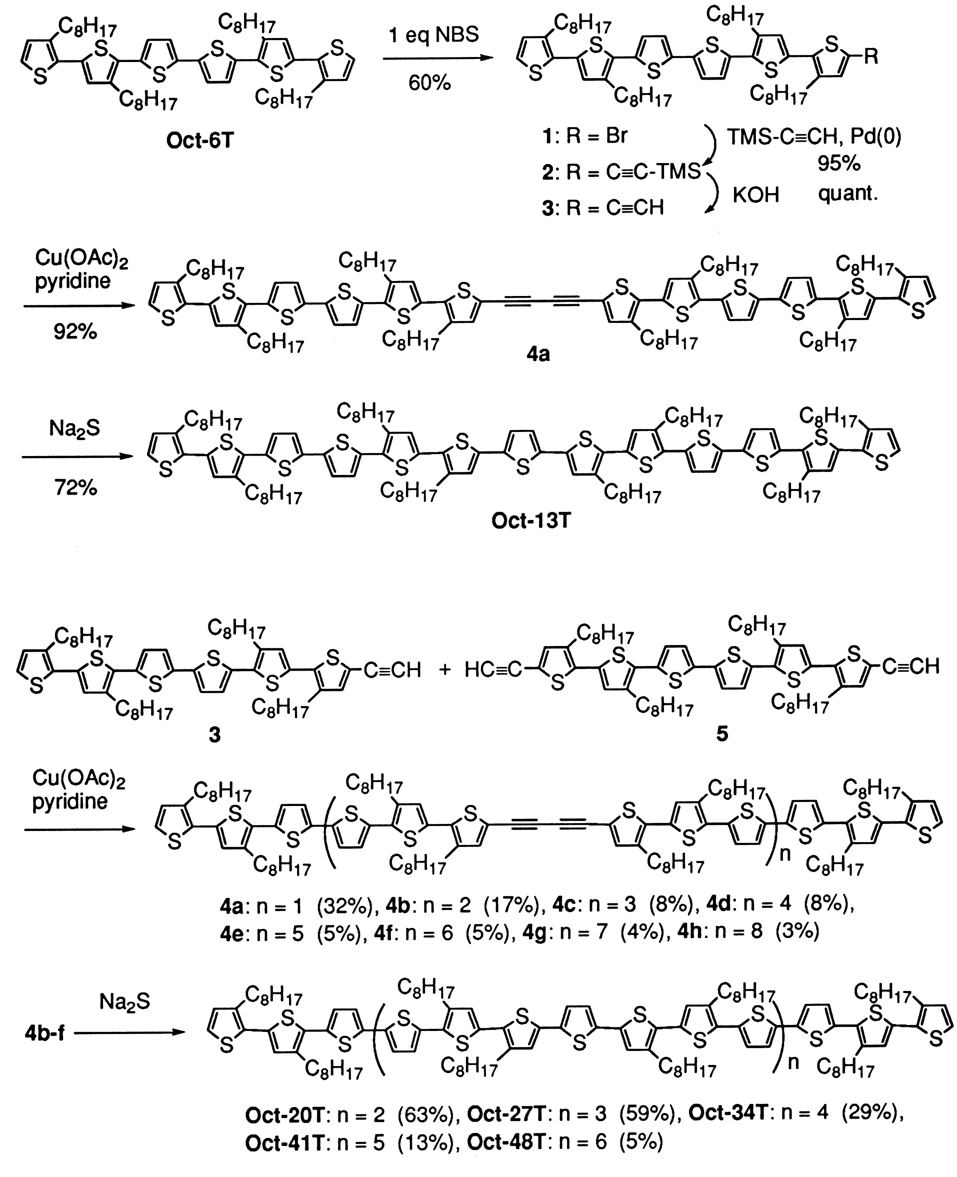
Dec-11T

Chart 1.



Scheme 1.

and mislinking through β-functionalization. The resulting byproducts are mostly impossible to remove from the desired oligomers, analogously to normal polymer syntheses. Thus only a few synthetic methods are available for the construction of long oligomers. The synthetic studies of oligothiophenes with more than ten thiophene units were begun in the early 1990s. As the first example, Wynberg et al. in 1991 reported the synthesis of the regioirregularly decyl-substituted 11-mer (**Dec-11T**, Chart 1), which was prepared by an iterative combination of the Stetter condensation and the following thiophene-ring construction induced by the Lawesson reagent.[5] A year later, Garnier et al. synthesized the regioirregularly decyl-substituted 12-mer (**Dec-12T**) by iterative oxidative coupling reactions of the decyl-substituted trimer (**Dec-3T**) with butyllithium, followed by $CuCl_2$, as shown in Scheme 1.[6] In 1994, Sato et al. succeeded in the one-step synthesis of a series of oligothiophenes, **Hex-6T**, **Hex-9T**, **Hex-12T**, and **Hex-15T**, with increasing intervals of three thiophene units by the reductive coupling of dihexyl-substituted dibromoterthiophene (**Hex-3T**).[7] The resulting oligomeric homologues were separated by preparative gel-permeation (size exclusion) liquid chromatography (GPLC). This approach is straightforward, although the yield of each product is very low, and higher homologues in the series can not be isolated because of their close sizes. Subsequently, Bäuerle et al. reported the two-step synthesis of the 16-mer (**Dod-16T**) from the didodecyl-substituted tetramer (**Dod-4T**) by Garnier's method.[8] On the other hand, we directly obtained a mixture of **Oct-10T** (25%), **Oct-15T** (8.4%), and **Oct-20T** (2.1%) by treating dioctyl-substituted quinquethiophene (**Oct-5T**) with the same reagents.[20] Thanks to a large difference in the molecular sizes due to an interval of dioctyl-substituted quinquethiophene segment, they were successfully separated from one another by a GPLC technique. The longest **Oct-20T** was, however, sparingly soluble in com-



Scheme 2.

mon solvents, making the examination of its inherent properties difficult.

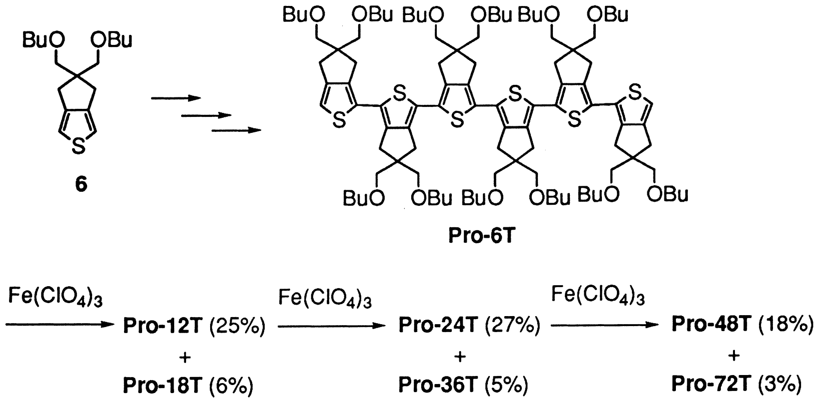
A drastic improvement in solubility is necessary in order to challenge even longer oligothiophenes. For this purpose, we focused on a key intermediate, tetraoctylsexithiophene (**Oct-6T**), where more alkyl groups serve to markedly enhance the solubility. Under its extension study, we adopted a combination reaction sequence of Eglinton coupling of ethynyloligothiophenes followed by sodium sulfide-induced 1,3-butadiyne cyclization (Scheme 2). Kagan et al. already used the same methodology for the synthesis of *α*-sexithiophene, which, however, involved the Glaser reaction in the initial coupling step.[21] Our reaction sequence has the advantage of avoiding the formation of analogous oligomeric by-products by undesired reactions. Thus, the treatment of **Oct-6T** with one equimolar NBS led to the formation of the monobromo derivative **1** (60% yield), which was subsequently reacted with trimethylsilylacetylene in the presence of the [Pd(PPh$_3$)$_4$] catalyst to give the trimethylsilylethynyl derivative **2** (95% yield), and **2** was then desilylated with potassium hydroxide to the ethynyl one **3** (quantitative yield). An Eglinton homo-coupling of **3** with copper(II) acetate in pyridine gave the bis(sexithienyl) diacetylene (**4a**) in 92% yield, of which the diacetylene moiety was reacted with sodium sulfide to produce **Oct-13T** in 72% yield.

For the shortened synthesis of higher oligomers, we used a random approach technique based on one-pot block polymerization. Thus, an Eglinton cross-coupling reaction using an equimolar mixture of the ethynyl derivative **3** and the diethynyl derivative **5**, similarly prepared from treatment of **Oct-6T** with two equimolar NBS, gave a mixture of a series of the oligo(sexithienylene-diethynylene)s **4a-h**, which were readily separated by preparative GPLC. Among them, the products **4b-f** like **4a** were converted with sodium sulfide to long oligothiophenes: **Oct-20T** (63%), **Oct-27T** (59%), **Oct-34T** (29%), **Oct-41T** (13%), and **Oct-48T** (5%).

When we attempted to prepare extraordinarily long oligothiophenes by a similar route starting from the above long oligothiophenes, we learned that selective functionalization at the terminal α-positions was impossible. The *α*-functionalization competes with *β*-functionalization, which is basically negligible for short oligomers, but noticeable for long oligomers owing to the statistical increase of the *β*-sites compared to the *α*-sites. The contaminated *β*-products are usually unremovable, thus leading to mislinking in the following coupling reactions. In order to avoid the formation of undesirable *β*-products, we used the *β*-blocked thiophene derivative **6** as a fundamental unit, in which a 2,2-bis(dibutoxymethyl)-1,3-propanediyl group was introduced into the two *β*-sites (Scheme 3).[16] After it was oligomerized to the 6-mer (**Pro-6T**) by the use of a conventional Stille coupling reaction, **Pro-6T** was subjected to oxidative coupling with iron(III) perchlorate to afford a mixture of **Pro-12T** (25%) and **Pro-18T** (6%). The isolated **Pro-12T** was again oxidized to give **Pro-24T** (27%) and **Pro-36T** (5%) under the same conditions. The reoxidation of **Pro-24T** gave **Pro-48T** (18%) and **Pro-72T** (3%). The **Pro-72T** thus obtained is the longest oligothiophene ever known.

2. Structures and Spectroscopic Properties of Long Oligothiophenes

The structures of long oligothiophenes like low-molecular homologues were unambiguously characterized by spectroscopic measurements. MALDI-TOF MS is especially effective in detecting the molecular ion peaks of all oligothiophenes; for example, **Pro-72T** showed a definite molecular ion peak corresponding to the molecular weight 21203. The ^{1}H NMR spectra are also very helpful for their structural characterization; for example, **Pro-72T** showed a small but specific signal due to the *α*-thiophene protons. In addition, all of the complex signals due to the *α*- and *β*-thiophene protons of **Oct-48T** were successfully assignable. It is worth noting that the molecular sizes of the present oligomeric series, measured by analytical GPLC using randomly shaped polystyrene standards, are evidently much inflated as compared to the actual ones, as shown in Fig. 1. This trend was already observed by Tour et al. for rod-shaped molecules, such as oligo(2,5-thienylene-ethynylene)s (**7**)[22] and oligo(para-phenylene-ethynylene)s (**8**).[23] In contrast, we observed that those of coil-shaped molecules, such as oligo(3,4-thienylene-ethynylene)s (**9**)[24] and oligo(2,3-thienylene-ethynylene)s (**10**)[25] are much deflated (Chart 2). Figure 1 also demonstrates that there is a good linear relationship of the actual molecular weights vs analytical GPLC ones for all the oligothiophene series and the oligo(sexithienylene-diethynylene) series. These results strongly



Scheme 3.

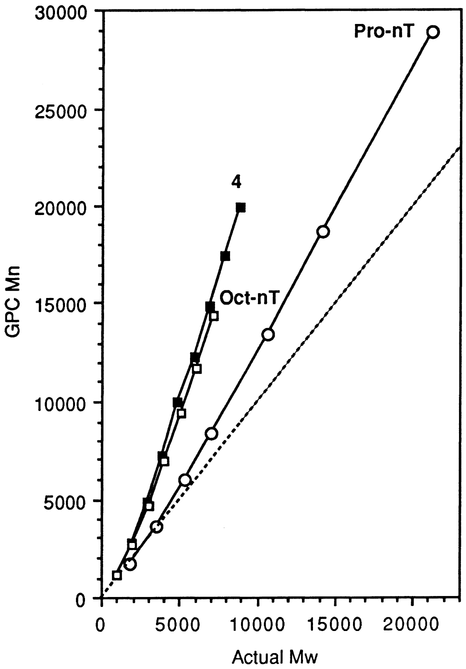


Fig. 1. Relationship of molecular weights determined by GPLC in THF using polystyrene standards versus the actual molecular weights of oligothiophenes (**Oct-nT** and **Pro-nT**) and oligo(sexithienylene-diethynylene)s (**4**).

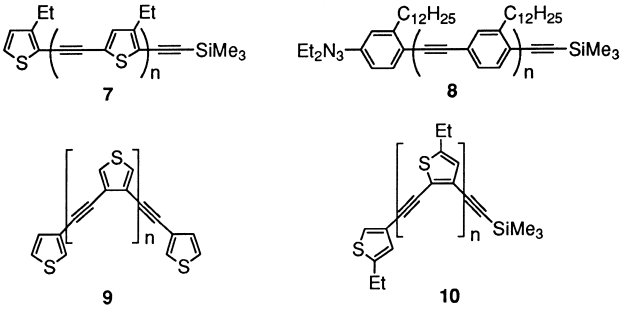


Chart 2.

suggest that the molecules of the present oligomeric series keep rigid rod shapes, even when the molecular chains are elongated. A molecular model with energetically favorable *all-trans* orientation with regard to the thiophene ring linkage indicates that **Oct-48T** has a length of 18.6 nm, the longest oligo(sexithienylene-diethynylene) (**4h**) a length of 25.0 nm, and **Pro-72T** a length of 27.9 nm. Since the other longest conjugated molecule so far known is 16.0 nm long for a co-oligomer of paraphenylene-ethynylene blocks and thienylene-ethynylene blocks,[26] these oligomers are of the longest class among fully conjugated π-systems.

In the electronic absorption spectra, the π–π* transitions of the **Oct-nT** series are progressively red-shifted and intensified with increasing chain length up to the 20-mer, as summarized in Table 1. There are no additional shifts of the absorption wavelength maxima from the 20-mer to the 27-mer. A similar chain-length dependence is also observed in the red shifts of their emission wavelengths. In the electronic absorption spectra of the **Pro-nT** series, however, it is recognizable that apparent red shifts continue up to the 24-mer: **Pro-6T**, λ_{max} 457.5 nm; **Pro-12T**, 505 nm; **Pro-18T**, 515 nm; **Pro-24T**, 520 nm; **Pro-36T**, 520 nm in CH_2Cl_2.[16] These results clearly indicate that a certain limitation on the extensive conjugation is around 20 thiophene units; such a limit is consistent with that previously suggested.[13]

The cyclic voltammograms of the **Oct-nT** series exhibit a broad redox wave due to the superposition of consecutive multi-step oxidation processes over a wide range of 0.5–1.2 V. Although the waves are ill-structured, the first oxidation peaks are distinguishable, and the peak potentials decrease with the oligomeric series (see also Table 1). Apparently, there is an appreciable difference in the oxidation potentials between the 27-mer and the 34-mer. Thus an effective conjugation length of the conjugated thiophene system in the oxidation state extends to around 30 thiophene units, which is much longer than in the neutral state.

3. Electrical Conductivities and Conduction Mechanism of Long Oligothiophenes

The cast films of the **Oct-nT** oligothiophenes are nearly insulating in the neutral state, but become conductive upon chemical doping with $FeCl_3$ in acetonitrile, with vaporized iodine, or electrochemical doping in acetonitrile containing tetrabutylammonium perchlorate as a supporting electrolyte (see also Table 1). The full doping level per thiophene unit is ca. 20% in any case. The conductivities of the 6-mer are in the wide range of 10^0–10^{-2} S cm^{-1}, varying according to the doping methods, while those of the longer oligomers are almost independent of the doping methods. There is evidently a progressive increase in conductivity from the 6-mer up to the 27-

Table 1. Electronic Spectra,[a)] Oxidation Potentials,[b)] and Conductivities of Oligothiophenes **Oct-nT**

Compd	λ^{abs}_{max}/nm	λ^{emis}_{max}/nm	E_{pa} /V	$\sigma^{c)}$/S cm^{-1}	$\sigma^{d)}$/S cm^{-1}	$\sigma^{e)}$/S cm^{-1}
Oct-6T	413	515, 549	0.78	1.2–3.0 (21%)[f)]	0.025–0.056 (20%)[f)]	0.62 (17%)[f)]
Oct-13T	453	567, 616	0.65	5.0–7.7 (23%)	3.2–3.7 (20%)	5.6 (23%)
Oct-20T	461	577, 622	0.55	11–21 (17%)	5.2–8.9 (17%)	9.7 (20%)
Oct-27T	461	577, 622	0.53	13–35 (16%)	12–25 (19%)	28 (22%)
Oct-34T	461	577, 622	0.49	12–36 (21%)	16–38	
Oct-41T	461	577, 622	0.48	22 (17%)		
Oct-48T	461	577, 622				

a) In tetrahydrofuran. b) vs Ag/AgCl in benzonitrile. c) $FeCl_3$ doping. d) I_2 doping. e) Electrochemical doping.
f) Doping level per thiophene unit.

mer, although the conductivity increase is not of a significant magnitude. The extension of the conjugated system is clearly advantageous to an enhancement of the conductivity. Interestingly, this change resembles the optical and voltammetric changes described above. It is worth noting that the converged conductivities (ca. 20 S cm^{-1}) of the long oligothiophenes are nearly equal to the value (17 S cm^{-1} for $FeCl_3$ doping) of poly(sexithiophene) (**11**, Chart 3). Apparently the effective conjugation length of approximately 20–30 thiophene units plays a critical role in determining the conductivities, in other words, the carrier transport of polythiophenes. It is natural to image that the film state of polythiophenes consists of fibrillar domains, and accordingly, carrier transport occurs by three processes, along the conjugated chains (intrachain process), among the stacked chains (interchain process), and via fibrillar contacts (interfibrillar process), as illustrated in Fig. 2. The chain extension is presumably effective for both intrachain processes and interchain processes but not so much for the interfibrillar processes, because the fibrilliar contact may be made through a limited area. The interfibrillar process is, however, the most crucial to the macroscopic conductivity of usual polythiophene film, since its morphological ordering results in a much higher conductivitiy, as found for regioregular head-to-tail polythiophenes.[2d,27] This is responsible for the small chain length dependence of the conductivity increase of oligothiophenes.

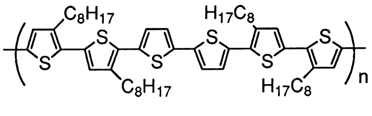


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Chart 3.

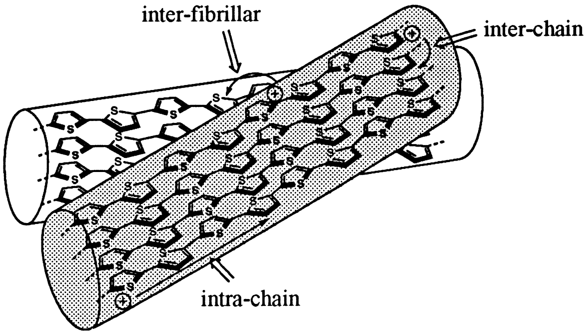


Fig. 2. Illustration for carrier transport of polythiophenes.

There have already been many reports about charge carriers in conducting polythiophenes. The doping level of about 20% simply means the presence of one radical cation (polaron) per five-thiophene unit, which was initially assumed as the principal carrier species.[28] However, the following silent ESR studies of conductive polythiophene films suggested spinless alternatives, such as the dications (bipolaron),[29] the π-stacked dimeric polarons (π-dimer),[30] and more recently the two individual polarons on a single chain (chain dimer) (Fig. 3).[31] In order to obtain deeper information on these carrier species, the oxidized species of the long oligothiophenes were generated by controlled addition of $FeCl_3$ in dichloromethane and monitored by ESR signal intensity and electronic absorption spectra. One-electron oxidation of **Oct-6T** demonstrates a strong ESR signal corresponding to the formation of the radical cationic species, while two-electron oxidation markedly decreases the ESR signal, indicating the formation of the dication species. On the other hand, one-electron oxidation of **Oct-13T** shows only 40% signal intensity compared to **Oct-6T**, followed by more decrease with further oxidation. Furthermore, oxidation of **Oct-20T** or **Oct-27T** makes ESR response in any oxidation state extremely weak. Evidently, spinless dimerized polarons are important in the long oligothiophene systems even in solution.[7d]

In the electronic absorption spectrum, the one-electron oxidation of **Oct-6T** causes the disappearance of the neutral π–π* transition and the alternative appearance of two absorption

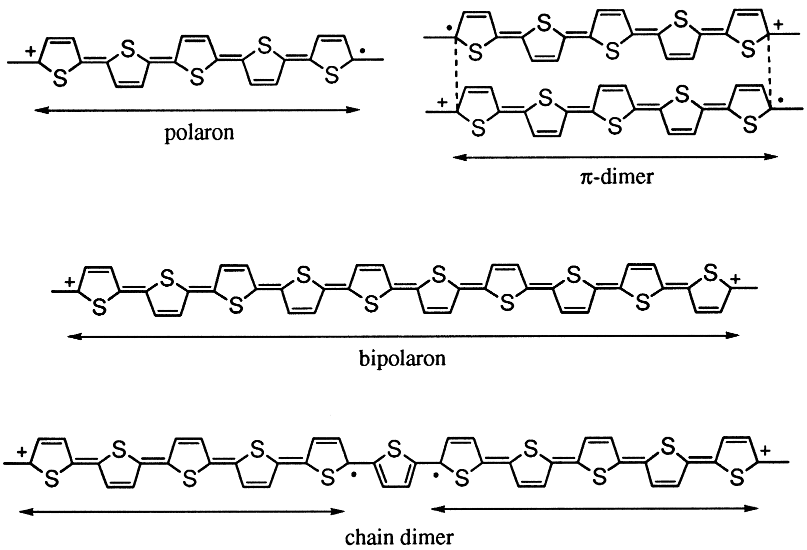


Fig. 3. Active charge carrier species for conductive polythiophenes.

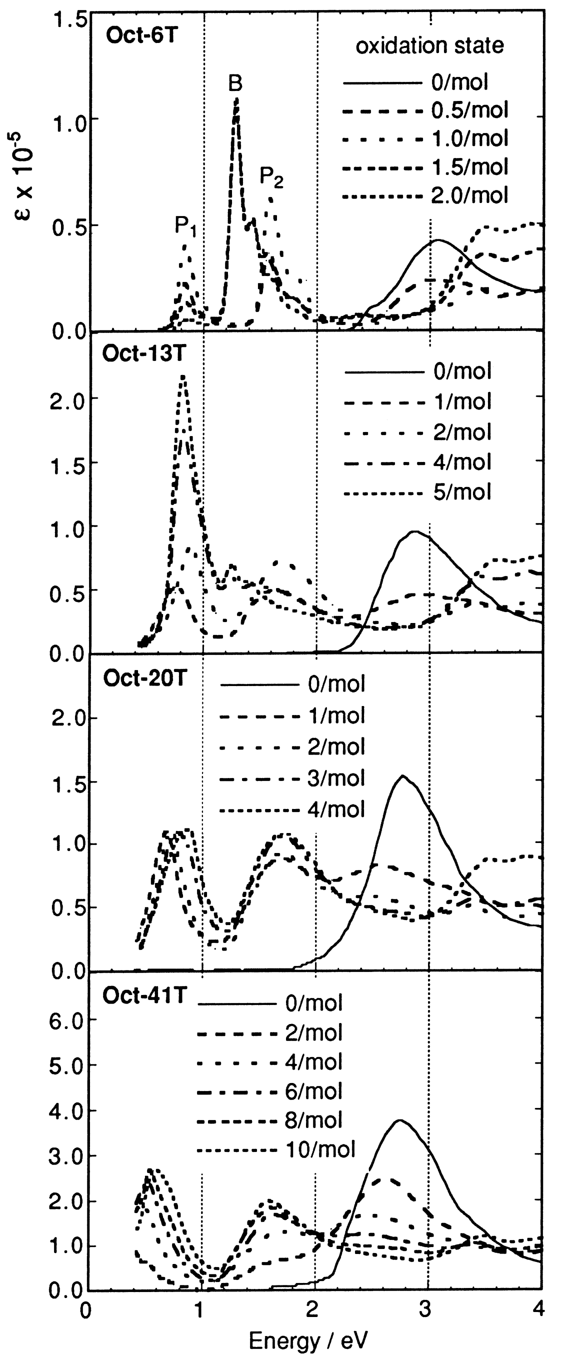


Fig. 4. Electronic absorption spectra of oligothiophenes under oxidation with $FeCl_3$ in dichloromethane.

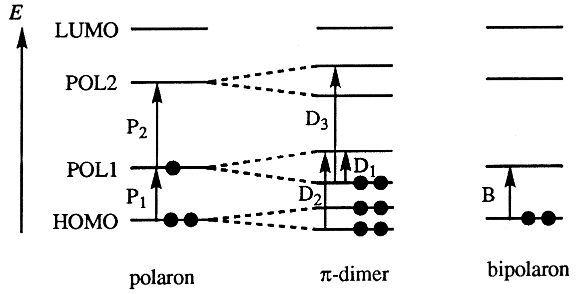
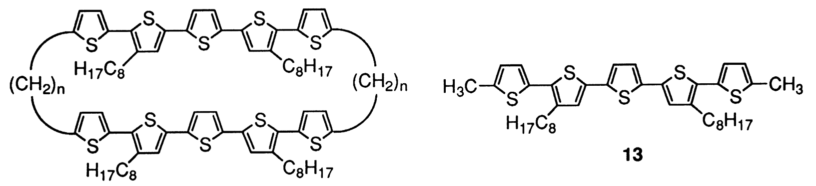


Fig. 5. Electronic transition diagrams for three oxidized species of oligothiophenes.

bands marked "P_1 and P_2" (0.83 and 1.58 eV) in the VIS/NIR region, whereas the two electron oxidation causes only one absorption band marked "B" (1.28 eV), as demonstrated in Fig. 4. These absorption patterns are characteristic of a polaron and a bipolaron, respectively, as explained by the electronic transition diagrams in Fig. 5.[32] Although **Oct-6T** can be oxidized to the bipolaron stage in the solution, the doping level (about 20%) of its film used for the conductivity measurement means that it is still at the polaronic stage. It has been already claimed that, in a condensed state, polarons exist as π-dimers.[30] The π-dimers are, however, evidenced principally by low temperature electronic spectra of doped oligothiophenes in solution, and it is usually difficult to distinguish the π-dimeric spectra from the polaronic spectra. In this regard, we have studied tetraoctyl-substituted [2.2]quinquethiophenophane (**12a**) and [3.3]quinquethiophenophane (**12b**),[33] which can be expected to behave as ideal π-dimer models, because the two oligomeric moieties are fixed closely by methylene bridges (Chart 4). In one-electron oxidation with $FeCl_3$ in dichloromethane, the spectrum of **12a** shows three absorption peaks in the vis/NIR region, as shown in Fig. 6. Of these, the high-energy band at 2.99 eV due to the non-oxidized quinquethiophene chromophore is identical to the absorption of neutral dimethyldioctylquinquethiophene (**13**). The remaining two low-energy bands (0.88 and 1.65 eV) due to the oxidized quinquethiophene are equal to those of the radical cationic species (polaron) prepared by mono-oxidation of **13**. Clearly there is no interaction between the two quinquethiophene moieties of **12a** in the one-electron oxidation state. However, in two-electron oxidation, the spectrum completely changes and gives three new bands at 0.89, 1.35, and 1.76 eV. The observation of the three bands strongly indicates the formation of a π-dimer from two monocationic species. The lack of much ESR response at the two-electron oxidation stage, differently from the one-electron oxidation, also supports the formation of a spinless dimer. Figure 5 also explains the origin of three transitions for a π-dimer, where the weak lowest-energy band (D_1) is due to an interchain transition. Easy intramolecular π-dimerization of the oligothiophenophane at ambient temperature strongly supports that polarons can exist as π-dimers in a condensed state. The controlled oxidations of **12b** demonstrate somewhat different spectral changes; in two-electron oxidation, only two strong bands at 1.00 and 1.85 eV, corresponding to D_2 and D_3 respectively, are observed. The absorption energies of the two bands are quite close to those (1.15 and 2.03 eV) detected for the intermolecular π-dimer of **13** at low temperature. This means that the [3.3]-system **12b** is a better π-dimer model than the [2.2]-system **12a**. In comparison with the rigid [2.2]-system **12a**, it is considered that the flexible [3.3]-system **12b** can effect a stronger π-dimeric interaction, giving rise to the red shift of the low energy band (D_2) and the blue shift of the high energy band (D_3). The weak interchain band (D_1) is concealed under the strong D_2 band.

For long oligomers with over 10 thiophene units or polythiophenes, on the other hand, one should consider the involvement of bipolarons and chain dimers besides π-dimers for the dimerized carrier species. The early one-electron oxidation of



12a : n = 2
12b : n = 3

13

Chart 4.

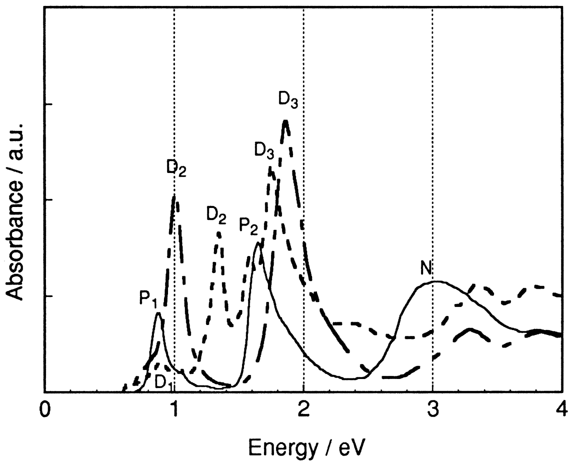
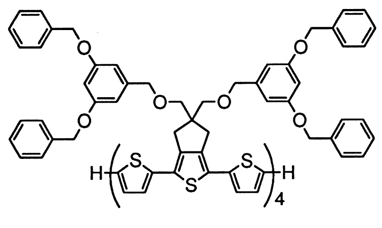


Fig. 6. Electronic absorption spectra of [2.2]- and [3.3]-quinquethiophenophanes in dichloromethane: **12a** under one-electron oxidation (——); **12a** under two-electron oxidation (----); **12b** under two-electron oxidation (———-).

Oct-13T shows two polaronic bands in the further longer wavelength region, which are gradually blue-shifted with the progress of oxidation (see also Fig. 4). The two-electron oxidation still retains the two bands (0.85 and 1.67 eV), and exhaustive oxidation leads to the appearance of a strong bipolaronic band (0.81 eV). Obviously the involvement of a bipolaron at the two-electron oxidation stage is ruled out. The longer oligothiophenes **Oct-20T**, **Oct-27T**, **Oct-34T**, and **Oct-41T** also demonstrate two bands during consecutive oxidation up to the about 20% doping level, reminiscent of the spectral behavior of polythiophene film.[34] Considering the ESR silence and selection rule, it is reasonable to assume that the two band species are π-dimers.[8,35] However, Janssen et al. recently proposed a chain dimer as an alternative for intramolecularly dimerized species,[10a,31] and Tol also supported its existence theoretically.[36] In order to obtain further information regarding this possible alternative, we have studied a dendron-pendent 12-mer (**Dendron-12T**, Chart 5), in which the dendrons can interfere sterically with the formation of π-dimers.[37] The two polaronic bands of **Dendron-12T** in the NIR region are also blue-shifted with oxidation and arrive at 0.75 and 1.52 eV after two-electron oxidation. Obviously the shifts are much smaller when compared to those for **Oct-13T**. This strongly suggests the formation of polaron-like dimeric species different from π-dimers and bipolarons. In the isolated oligothiophene, the chain dimers proposed by Janssen et al. must be involved.



Dendron-12T

Chart 5.

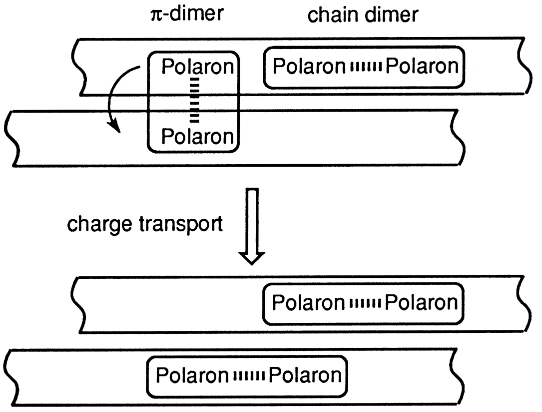
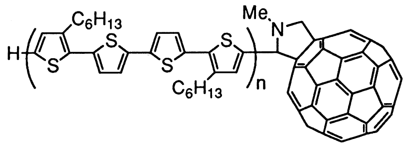


Fig. 7. Illustration for carrier transport through the transfiguration from a π-dimer to a chain dimer.

From the above results, it can be speculated that the two oxidation bands observed for conductive oligothiophenes and polythiophenes are the superposition of the two bands due to π-dimers and chain dimers, and that both are the active charge carrier species. One may properly imagine that charge transport occurs through the transfiguration of both species; more specifically, the interchain process is regarded as a combination of dissociation from either π-dimers or chain dimer to polarons, hopping of the latter across the adjacent chains, and finally recombination to the dimeric species (Fig. 7). The relatively low conductivity of **Oct-6T** is explained by its short conjugation length, which is too tight to accommodate a chain dimer. The oligo(sexithienylene-diethynylene) series showed $FeCl_3$-doped conductivities of the order of 10^{-1} S cm^{-1}, which were very similar to that of **Oct-6T** and independent of the chain length: **4a**, 0.4 S cm^{-1}; **4b**, 0.07 S cm^{-1}; **4c**, 0.1 S cm^{-1}. This can be rationalized in terms of less effective conjugation of the oligo(sexithienylene-diethynylene)s which must disallow the involvement of the chain dimer species spreadable over a diethynylene spacer.

4. Oligothiophene-Based Energy- and/or Electron-Transfer Systems

It is of particular interest to know how effectively long oligothiophenes serve as molecular wires for electron- and/or energy-transfer. As the first step of our efforts directed to oligothiophene-based electronic devices, we have studied a series of fullerene-linked oligothiophenes **nT-C60**, in which the [60]fullerene is covalently bonded to the oligothiophene (Chart 6).[38] In such electron donor/C_{60} dyad systems, fullerene can behave as an effective acceptor for intramolecular energy- or electron-transfer.[39] The electronic absorption spectra of these dyad systems consist of superposition of the electronic transitions of the oligothiophene and fullerene chromophores, meaning no interaction between the two chromophores in the ground state. In contrast, both chromophores are markedly interactive in the excited state. The emission spectrum of **4T-C60** in toluene, even when the oligothiophene chromophore is excited, demonstrates only weak fluorescence at around 700 nm, assigned to an emission from the fullerene chromophore, as shown in Fig. 8. On the other hand, **8T-C60** and **12T-C60** show dual fluorescence not only from the fullerene chromophore, but also from the oligothiophene chromophore. However, the quantum yields (Φ_f) of the oligothiophene fluorescence are drastically reduced by a factor of 100–1000 as compared to those of the nonlinked oligothiophenes. Obviously there is rapid intramolecular singlet–singlet energy transfer from the oligothiophene moiety to the fullerene. Based on the fluorescence quantum yields and the singlet state life times, it can be estimated that the rate constants of the intramolecular energy transfer processes are on the picosecond time scale: **4T-C60**, $k_{et} > 10^{12}$ s^{-1}; **8T-C60**, 10^{12} s^{-1}; **12T-C60**, 2×10^{11} s^{-1}.



4T-C60 : n = 1
8T-C60 : n = 2
12T-C60 : n = 3

Chart 6.

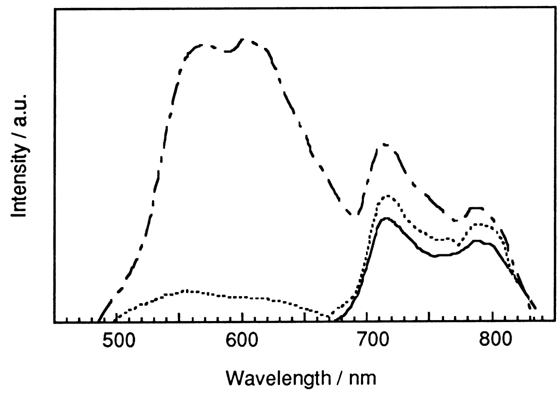
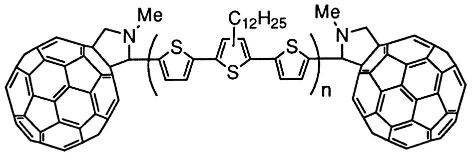


Fig. 8. Fluorescence spectra of **4T-C60** (——), **8T-C60** (----), and **12T-C60** (— — —) in toluene.



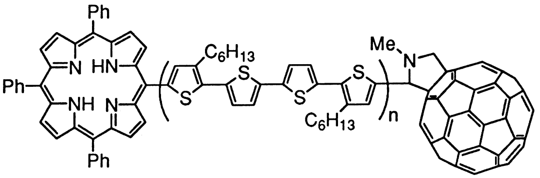
C60-nT-C60 : n = 1, 2, 3

Chart 7.

In the photophysical investigation of **C60-nT-C60** triads (Chart 7) in toluene, Janssen et al. observed similar fast energy transfer from the central oligothiophene moiety to either of the fullerenes with rate constants ranging between 10^{12} and 10^{13} s^{-1}.[40]

Further careful time-resolved absorption and emission measurements of **4T-C60** dyad have revealed that the decay process is markedly solvent-dependent.[41] In nonpolar toluene, only the intramolecular energy transfer is observed, whereas in polar solvents such as benzonitrile and THF, charge separation occurs at a rate constant on the order of 10^{10} s^{-1}. The quantum yield for the charge separation is nearly unity. Interestingly, the resulting charge-separated state has an unprecedentedly long lifetime of microsecond order. Thus the fullerene-oligothiophene dyad is an intriguing photoinduced charge separation system.

As the advanced step, we have studied the porphyrin/oligothiophene/fullerene triad system **Por-nT-C60**, for which intramolecular energy- or electron-transfer via the oligothiophene spacer from the porphyrin to the fullerene can be expected (Chart 8).[42] Actually, when the porphyrin chromophore



Por-4T-C60 : n = 1
Por-8T-C60 : n = 2
Por-12T-C60 : n = 3

Chart 8.

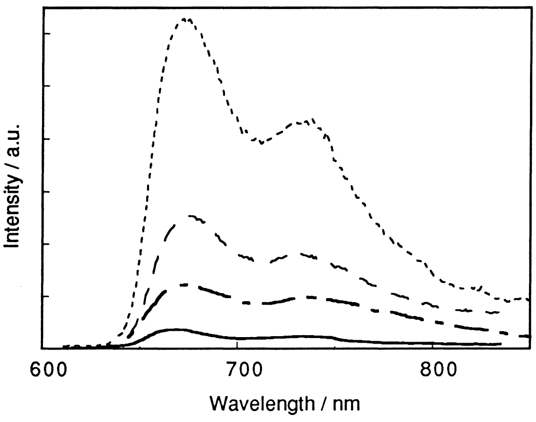


Fig. 9. Fluorescence spectra of **Por-4T-C60** (——), **Por-4T** (----), **Por-8T-C60** (— — —), and **Por-8T** (— — —) in benzonitrile.

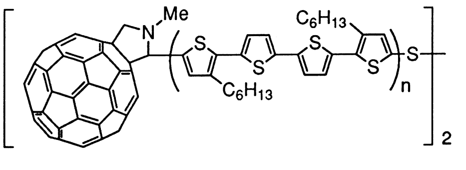
is excited in benzonitrile, 95% of the porphyrin fluorescence from **Por-4T-C60**, 46% from **Por-8T-C60**, and 21% from **Por-12T-C60** as compared to the respective porphyrin-linked oligothiophenes **Por-nT** are quenched by the additionally attached fullerene (Fig. 9). A considerable amount of electron transfer might occur from the porphyrin moiety to the fullerene. The rate constants for quenching are as follows: **Por-4T-C60**, k_q 5.7 × 10^9 s^{-1}; **Por-8T-C60**, 6.2 × 10^8 s^{-1}; **Por-12T-C60**, 2.0 × 10^8 s^{-1}. The small distance dependence of the electron transfer (attenuation factor 0.1 $Å^{-1}$) suggests that oligothiophenes can function as a long-range molecular wire.[43]

5. Oligothiophene-Based Photovoltaic Devices

The discovery of highly efficient photoinduced electron transfer for **nT-C60** has prompted us to investigate the application of oligothiophenes as molecular wires to a photovoltaic cell. The optoelectronic devices of donor-acceptor linked photoactive molecules ordered on a metal electrode by a self-assembled monolayer (SAM) technique receive current attention.[44] As a new type of photoactive molecule, we have studied the [60]fullerene-linked oligothiophene disulfides (**C60-nT-S**)$_2$ (Chart 9), where the disulfide serves as an anchoring group for SAM on a gold electrode.[45] Monolayers were prepared by immersion of the Au(111)/mica substrate in saturated chloroform solution of (**C60-nT-S**)$_2$, and the adsorbed amount of **C60-nT-S** on Au was estimated from the charge of the reduction peak of the fullerene moiety in the voltammogram. The different occupied areas of the **C60-4T-S** molecule (750 $Å^2$ $molecule^{-1}$) and the **C60-8T-S** molecule (180 $Å^2$ $molecule^{-1}$) suggest that the former lies down on the gold surface, while the latter stands straight on the gold surface, as illustrated in Fig. 10.

Photoelectrochemical measurements were performed in an argon-saturated 0.1 mol dm^{-3} Na_2SO_4 solution containing 5 × 10^{-3} mol dm^{-3} methyl viologen (MV^{2+}) as an electron carrier using the modified Au electrode as a working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode. In the visible region, the absorption due to the oligothiophene is much stronger as compared to that of the fullerene, and accordingly, the oligothiophene is a major absorber of visible photons. Under illumination of 440 nm light, the Au/**S-8T-C60**/MV^{2+}/Pt cell showed a marked photoelectrochemical response, as shown in Fig. 11. An increase in the cathodic photocurrent with an increase of the negative bias to the gold electrode demonstrates that electrons flow unidirectionally from the gold electrode to the counter electrode through the photoactive molecular wire, as depicted in Fig. 12.

In contrast, the Au/**S-4T-C60**/MV^{2+}/Pt cell scarcely responded to the visible light. The lack of the photocurrent for this device is ascribable to the lying structure of the **C60-4T-S** moiety on the gold surface. It is thus desirable to use a self-reliant molecule for SAM. For this purpose, we have next de-



(C60-4T-S)$_2$: n = 1
(C60-8T-S)$_2$: n = 2

Chart 9.

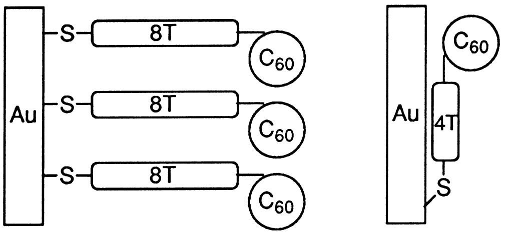


Fig. 10. Illustration for SAMs of **C60-4T-S**/Au and **C60-8T-S**/Au.

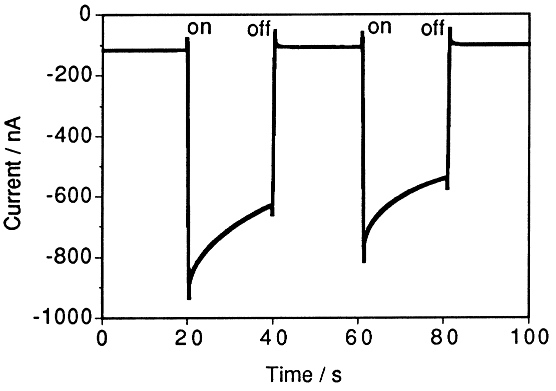
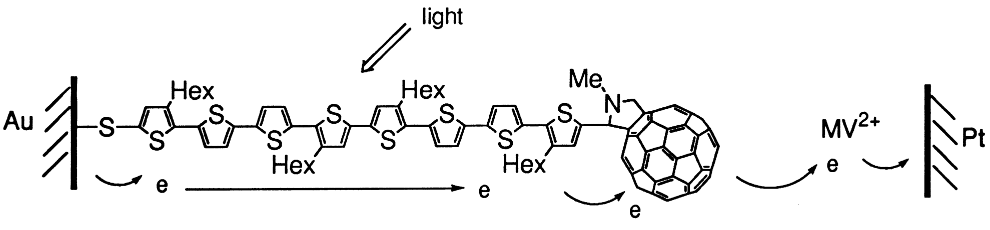
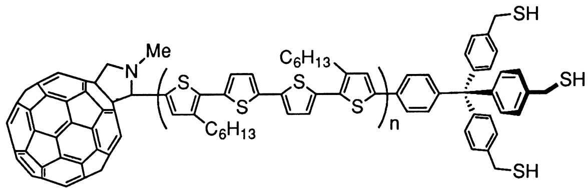


Fig. 11. Photoelectrochemical response for Au/**S-8T-C60**/ MV^2+/Pt device, when a 440 nm light (22 mW cm^{-2}) is on and off.



Au/S-8T-C60

Fig. 12. Illustration for an electron flow in Au/**S-8T-C60**/MV^{2+}/Pt device.



C60-4T-AnchorSH : n = 1
C60-8T-AnchorSH : n = 2

Chart 10.

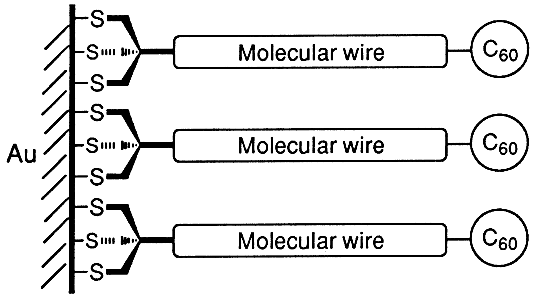


Fig. 13. Illustration for SAM of **C60-4T-AnchorS**/Au.

signed **C60-nT-AnchorSH** molecules (Chart 10), where the anchoring tripod serves for three-pointed standing on the gold surface.[46] The similarly prepared Au/**AnchorS-4T-C60**/MV^{2+}/Pt cell produced considerable photocurrent response, roughly comparable to that of the above Au/**S-8T-C60**/MV^{2+}/Pt cell. Obviously the **C60-4T-AnchorS** molecule stands by itself perpendicularly to the gold surface, as illustrated in Fig. 13. Interestingly, the Au/**AnchorS-8T-C60**/MV^{2+}/Pt cell showed larger photocurrent by a factor of 2–3 than the **C60-4T-AnchorS**-made cell. This indicates that long oligothiophenes are promising as charge-carrying molecular wires as well as donor building blocks for molecular photoelectric systems.

6. Concluding Remarks

Significant developments of structurally well-defined, extraordinarily long α-oligothiophenes corresponding to monodisperse polymers have been attained in terms of their promising optical and conductive properties. The systematic studies of these long oligomers have been very helpful for the elucidation of effective conjugation length, carrier transport, and carrier species of conductive polythiophenes, which were previously obscure and controversial. In addition, from the optical studies of oligothiophene-including dyad and triad systems, it has turned out that long oligothiophenes are also useful as molecular wires for efficient energy- and/or electron-transfer systems. They are thus among the most potential components for future molecular-scale electronic devices. In designing such devices, however, the problem of how oligothiophenes can be introduced into nanoarchitectures still remains to be solved. As finally demonstrated in the section of oligothiophene-based photovoltaic devices, SAMs would provide a powerful technique for the interface.

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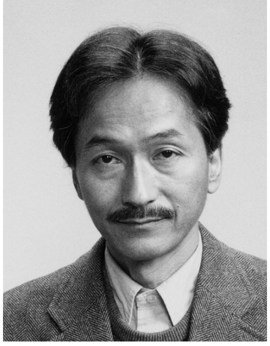
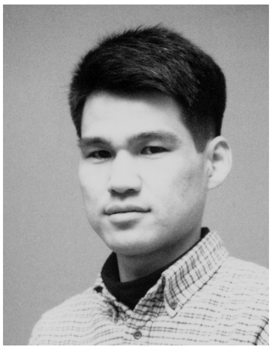
Tetsuo Otsubo was born in Osaka in 1942, and received his B.Sc. (1966) and M.Sc. (1968) from Osaka University. He started his academic career as a research associate at the same University, where he studied cyclophane chemistry with Prof. S. Misumi and received his Ph.D. in 1972. He spent a postdoctral visit to University of Oregon, U.S.A., in the research group of Prof. V. Boekelheide from 1974 through 1976. In 1979, he joined the Prof. F. Ogura's group of Hiroshima University, where he was promoted to associate professor in 1980. Since 1992, he has served as full professor in the Department of Applied Chemistry of the same university. His current research projects focus on the developments of novel organic conductors and molecular wires. He is the author of more than 230 publications.



Yoshio Aso was born in Fukuoka in 1953. He graduated from the Department of Chemistry, Faculty of Science, Osaka University in 1977, and received his Dr. of Science degree in 1983 from Osaka University for research with Prof. M. Nakagawa. He joined the group of Prof. R. Noyori and Prof. Y. Hayakawa at Nagoya University in 1981, and then moved to Hiroshima University as a research associate to join the group of Prof. F. Ogura in 1983. After postdoctoral research with Prof. L. T. Scott at University of Nevada Reno and at Boston College from 1992 to 1994, he was promoted to associate professor at Hiroshima University in 1994. From 1998 to 2000, he worked at Institute for Fundamental Research of Organic Chemistry, Kyushu University, as associate professor. His research interests include the synthetic, structural, and physical chemistry of electron- and photo-functional organic materials.



Kazuo Takimiya was born in Hiroshima in 1966 and received his Doctorate of Engineering from Hiroshima University in 1994 under the supervision of Prof. Ogura. He was a fellow of the Japan Society for the Promotion of Science (JSPS) for Junior Scientists from 1993 to 1994, and then has joined the Prof. T. Otsubo's group as a research associate since 1994. From 1997 to 1998, he worked as a postdoctoral fellow in Prof. J. Becher's group in Odense University, Denmark. His current interests focus on the development of organic functional materials based on organic synthesis.