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Functional oligothiophenes as advanced molecular electronic materials

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The oligothiophene/fullerene dyad system shows marked photoinduced electron transfer from the oligomer to the attached fullerene at the terminal position, and is successfully put to practical use in the fabrication of photovoltaic cells. The further modified dyad system, attaching a thiol or disulfide anchoring group at another terminal position, can form a self-assembled monolayer (SAM) on a gold substrate, where the tethered molecules are unidirectionally ordered. In particular, the use of a tripodal anchoring group provides a powerful approach for the formation of a much denser and more stable SAM, which is beneficial for the high performance of SAM-based photovoltaic cells. The porphyrin/oligothiophene/fullerene triad system is designed to evaluate efficient intramolecular electron transfer from the terminal porphyrin to the other terminal fullerene through the central oligothiophene, revealing the high potential of oligothiophene as a long-range molecular wire. Other oligothiophenes incorporating pyrenes or terpyridines are developed as light-emitting materials useful for electroluminescent (EL) devices. In these devices, the pyrene-modified system also acts as a hole-transport layer, whereas the terpyridine-modified system acts as an electron-transport layer.

1. Introduction

Structurally well-defined conjugated nanoscale molecules have attracted much current attention in terms of molecular electronic materials.[1] Such molecules are finding various applications in electrical conductors,[2] photovoltaic cells,[3] electroluminescent (EL) devices,[3,4] non-linear optics,[5] and field effect transistors.[6] In addition, they are expected to serve as promising molecular wires that will be indispensable to forthcoming single molecule electronic devices.[7] Recent improved synthetic techniques have allowed the appearance of even single-component molecules with lengths of more than 10 nm, suitable for nanoarchitecture. Among such nanomolecules, the most progressive is a family of highly conjugated α-linked oligothiophenes, which have two great advantages in synthetic research.[1g,8] One is to be relatively readily extended to very long oligomers. For example, we recently succeeded in the synthesis of a series of oligothiophenes up to 48 mer with a length of 18.6 nm.[2c] As is the case for polymers, the study of such long oligomers is hampered by insolubility. This can be overcome by introduction of solubilizing groups into the side β-positions of the oligothiophenes. Long oligothiophenes retain rigid rod structures as the chains increase, and accordingly their effective conjugation lengths extend over 20–30 thiophene units. The high conjugation causes marked red-shifts of their electronic absorption and emission transitions to the visible region, considerably lowering their oxidation potentials and high stabilization of the resulting radical cationic species, all of which are beneficial for electronic materials. The other synthetic advantage is to be appropriately functionalized at the terminal α-positions or the side β-positions. Suitable modifications of their molecular structures with electro- or photo-active groups should permit oligothiophenes to be transformed to more intelligent systems that may find a number of applications for use in electronic and optoelectronic devices.

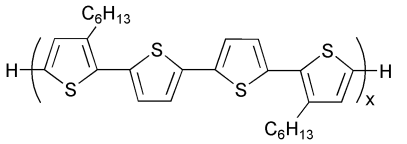
With wide interest in the development of oligothiophene-based devices, our group has recently devoted its efforts to the functionalization of long oligothiophenes using covalent linkages with versatile electro- or photo-active compounds such as fullerenes, porphyrins, pyrenes and terpyridines. Herein, we review the electro- and photo-physical characteristics of functional oligothiophenes, which are mostly derived from hexyl-substituted oligothiophenes **1** (Chart 1, abbreviated as ***n*T**), together with their applications as advanced materials for photovoltaic cells and EL devices.

2. Oligothiophene/fullerene dyad systems

Photoinduced electron or energy transfer is a key function for the construction of optoelectronic devices or artificial photosynthetic systems.[9] As the first step of our efforts directed to the development of oligothiophene materials with such a function, we studied fullerene-linked oligothiophenes **3** (abbreviated as ***n*T-C$_{60}$**), in which the [60]fullerene is covalently bonded to the terminal position of oligothiophenes.[10] In such electron donor/fullerene dyad systems, the fullerene can behave as an effective acceptor for intramolecular electron or energy transfer.[11] The synthesis of **3** was accomplished by the Vilsmeier reaction of **1** to give the aldehydes **2**, followed by treatment with fullerene and *N*-methylglycine (Prato method),[12] as shown in Scheme 1.

The electronic absorption spectra of these dyad systems, as demonstrated in Fig. 1, consist of a superposition of the electronic transitions of the oligothiophene **1** (a strong absorption at 400–500 nm) and the [60]fullerene adduct **4** (see Chart 2) (a strong absorption at around 330 nm tailing up to 700 nm). This means that although the two chromophores are closely linked to each other, there is no interaction between them in the ground state. In contrast, both chromophores markedly interact in the excited state.

Oligothiophenes **1** show strong fluorescence in the visible region of 500–700 nm. However, the emission spectrum of **4T-C$_{60}$** in toluene, even when the oligothiophene chromophore



1 (nT), x = 1–4

Chart 1 Hexyl-substituted oligothiophenes.

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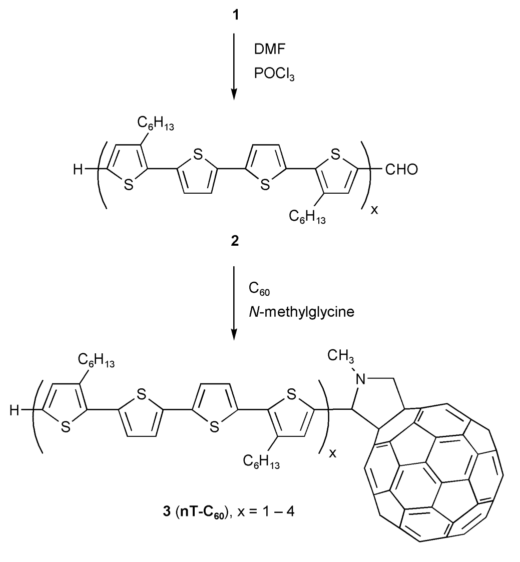

Scheme 1 Synthesis of oligothiophene/fullerene dyads **3**.

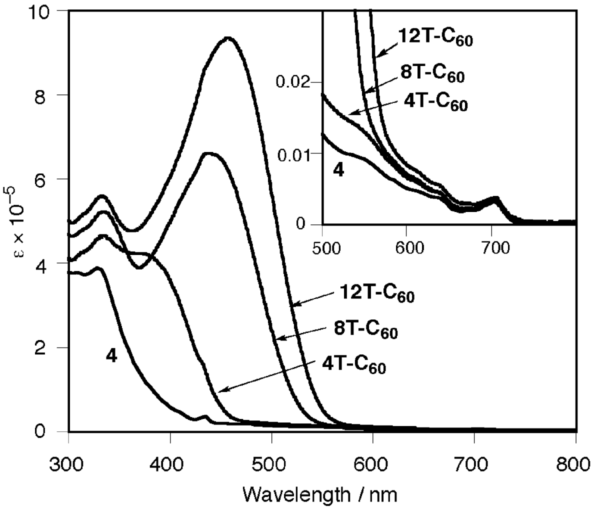

Fig. 1 Electronic absorption spectra of *n*T-C_{60} in toluene.

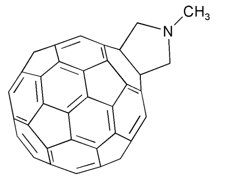

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Chart 2 The [60]fullerene adduct **4**.

is excited, no longer demonstrates direct fluorescence from the oligothiophene moiety (Fig. 2). Alternative weak fluorescence is observed around 700 nm, assignable to an emission from the fullerene chromophore. This result obviously indicates that in the dyad there is fast intramolecular singlet–singlet energy transfer from the excited oligothiophene moiety to the fullerene. On the other hand, **8T-C_{60}** and **12T-C_{60}** show dual fluorescence not only from the fullerene chromophore, but also from the oligothiophene chromophore. In the photophysical decay processes of the long oligothiophene-containing dyads, energy transfer becomes slow and, as a result, competes with direct fluorescence. However, energy transfer is still predominant, because the quantum yields (Φ) of fluorescence from the oligothiophenes are drastically reduced by a factor of 10^2–10^3 as compared to those of non-linked oligothiophenes **1**. Based on the fluorescence quantum yield and the singlet state lifetime, it can be evaluated that the rate constant of the intramolecular energy-transfer process is on the picosecond timescale and gradually decreases with the chain length of the oligothiophene, that is, the increasing separation of the two chromophores.

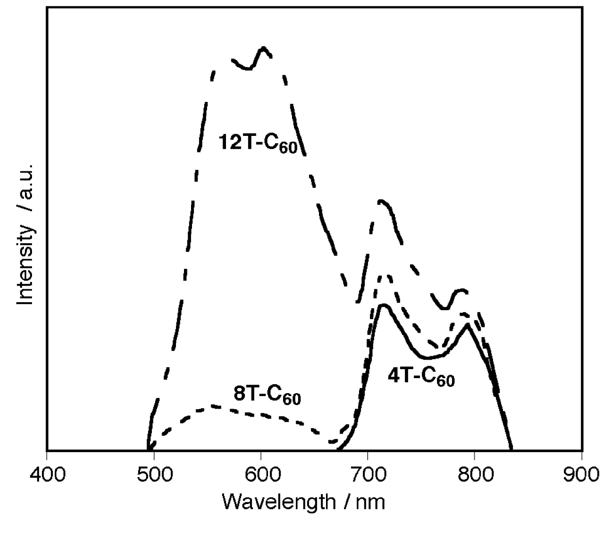


Fig. 2 Emission spectra of *n*T-C_{60} in toluene.

Further careful time-resolved absorption and emission measurements of **3** have revealed that the decay process is markedly solvent-dependent.[13,14] In the fluorescence spectra in polar solvents such as benzonitrile and THF, no emission from the fullerene chromophore is observed, quite different from the above spectral behavior in non-polar toluene. This is interpreted in terms of intramolecular electron transfer from the oligothiophene moiety to the fullerene, and is evidenced by the observation of a transient absorption due to the radical cation species of the oligothiophene. It is considered that solvation by polar solvents stabilizes the charge-separation state much more than the energy-transfer state, and as a result, electron transfer predominantly occurs. The quantum yield for the charge-separation process is nearly unity. The photophysical energy diagram for **8T-C_{60}** is illustrated in Fig. 3.

Different from the energy transfer, the electron transfer of **8T-C_{60}** or **12T-C_{60}** occurs more rapidly than that of **4T-C_{60}**, because the lower oxidation potential of the longer oligothiophene is more effective at lowering the energy level of the

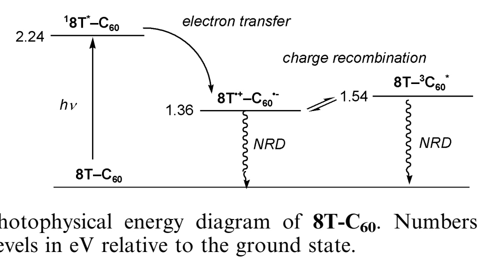
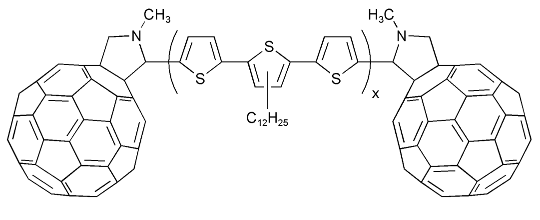


Fig. 3 Photophysical energy diagram of **8T-C_{60}**. Numbers indicate energy levels in eV relative to the ground state.



5, x = 1 – 3

Chart 3 Oligothiophene/fullerene triads **5**.

charge-separated state.[14] From the viewpoints of their easy photoinduced electron transfer as well as intense absorption in the visible region, the long oligothiophene/fullerene dyads have a potential for superior photosystems that may be applicable to light-energy conversion cells. In the photophysical investigation of triads **5** (Chart 3), Janssen *et al.* observed similar fast energy transfer in a non-polar solvent[15] and electron transfer in a polar solvent[16] from the central oligothiophene moiety to either of the two terminal fullerenes.

3. Porphyrin/oligothiophene/fullerene triad systems

Photoactive triad systems, in which a donor and an acceptor are separated by a molecular spacer, are of current interest in terms of nanoarchitecture associated with molecular transmitters, memories, switches and sensors.[17] It is generally known that the efficiency of electron transfer through a molecular wire decreases exponentially with the increasing length of the wire, and the attenuation factor in the exponential is closely related to the electronic structure of the molecule constituting the wire.[18] Much synthetic and theoretical research has thus been devoted to finding molecular systems which allow long-range electron or energy transfer.[19] The high conjugation of oligothiophenes is expected to make them promising candidates for long-range molecular wires.[20] An oligothiophene-including triad system is thus interesting as a model for conveniently evaluating the performance of an oligothiophene wire (Fig. 4).

As the first example of such triad systems, Effenberger and co-workers reported anthryloligothienylporphyrin (**6**)[21] and anthryloligothienylfullerene (**7**),[22] see Chart 4, in which photoinduced electron or energy transfer smoothly occurred from the excited anthracene as a donor to the porphyrin or fullerene as an acceptor *via* the oligothiophene spacer. However, the spacer was limited to only short oligomers up to 5 mer, so that the distance dependence of the efficiency remained unsolved.

Extending our study of the dyad system **3**, we recently designed a novel triad system **10**, which comprises three components of porphyrin, oligothiophene and fullerene.[23] Its synthesis was carried out as shown in Scheme 2, where the porphyrin/oligothiophene dyads **8** were first prepared from the formyloligothiophenes **2** by the Lindsey method,[24] and then converted to **10** by the same method used for the synthesis of **3**.

The electronic absorption spectra of **10** demonstrate that there is no electronic interaction among the three components in the ground state. On the other hand, the emission spectra show an interactive feature. When the porphyrin chromophore is excited in benzonitrile, 95% of the porphyrin fluorescence for the quaterthiophene system ($x = 1$), 46% for octithiophene ($x = 2$) and 21% for dodecithiophene ($x = 3$) as compared to the respective porphyrin-linked oligothiophenes (**8**) are quenched by the attachment of the additional fullerene. There is no appreciable emission from the fullerene, which indicates that a substantial amount of electron transfer occurs from the porphyrin moiety to the fullerene through the oligothiophene spacer. On the basis of the quenching rates and the fluorescence lifetimes, it can be estimated that the rate constants for electron transfer reaction (k_{ET}) are on the nanosecond timescale: **10** $x = 1$, $5.7 \times 10^9\ \mathrm{s}^{-1}$; $x = 2$, $6.2 \times 10^8\ \mathrm{s}^{-1}$; $x = 3$, $2.0 \times 10^8\ \mathrm{s}^{-1}$. The donor–acceptor distances (R_{DA}) are 1.4 nm for **10** $x = 1$, 3.0 nm for $x = 2$ and 4.6 nm for $x = 3$. A plot of the rate constant *vs.* the distance gives a good straight line according to the equation $k_{\mathrm{ET}} = A\exp(-\beta R_{\mathrm{DR}})$. From the slope of the line, an attenuation factor $\beta = 0.11$ Å^{-1} is obtained. This value for electron transfer is much smaller than the attenuation factor $\beta = 0.6$–1.2 Å^{-1} for saturated hydrocarbon bridges[25] and 0.32–0.66 Å^{-1} for conjugated paraphenylenes,[26] and comparable to the 0.04–0.2 Å^{-1} for oligoenes[18,27] and 0.04–0.17 Å^{-1} for oligoynes.[27b,28] Thus this result shows that oligothiophenes can serve as superior molecular wires allowing an efficient long-range electronic coupling between the donor and the acceptor, similarly to oligoenes and oligoynes. Because extraordinarily long oligothiophenes are accessible, and because of their high thermal stabilities relative to oligoenes and oligoynes,[2] oligothiophenes are certainly qualified as the long-distance molecular wires of choice.

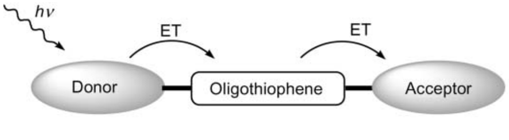


Fig. 4 Photoinduced electron or energy transfer *via* an oligothiophene wire.

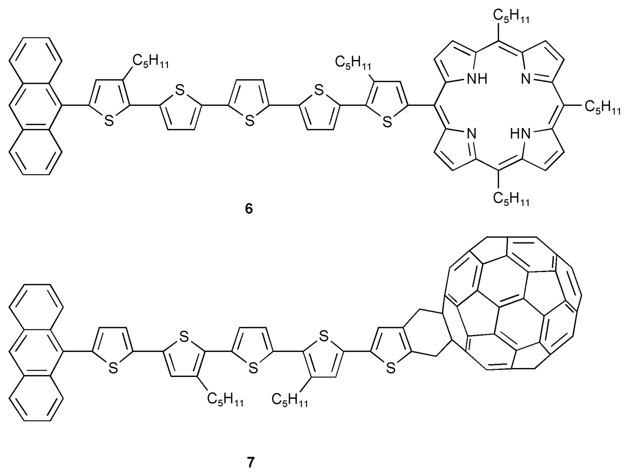
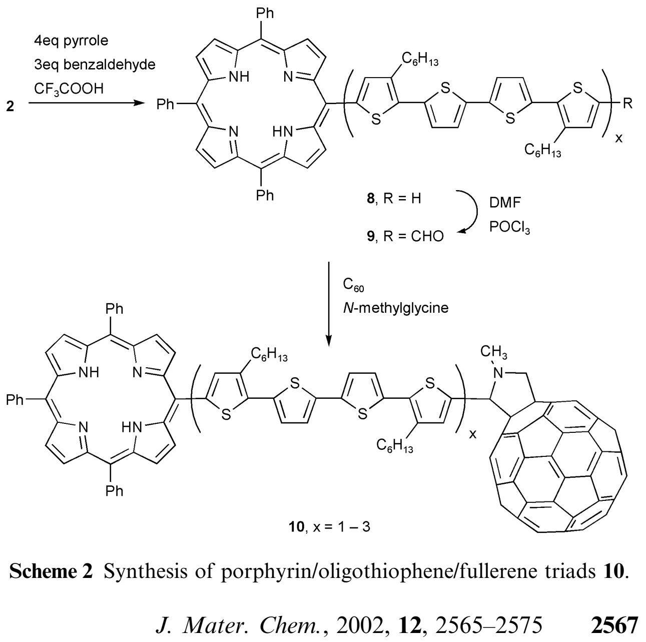


Chart 4 Donor/oligothiophene/acceptor triads.



Scheme 2 Synthesis of porphyrin/oligothiophene/fullerene triads **10**.

4. Incorporation of oligothiophene/fullerene dyads in photovoltaic devices

Efficient photoinduced electron transfer from a conjugated polymer to a fullerene[29] has found application in low-cost plastic solar cells.[30] Early devices containing both components in a bilayer type yielded only low performance for power conversion,[31] but modified bulk heterojunction devices using a blend of both components in the active organic layer markedly improved solar power efficiencies,[32] which were recently enhanced up to 2.5%[33] for the best class of organic solar cells.[30b,34] Nevertheless, such organic solar cells are still far inferior to conventional inorganic solar cells that routinely demonstrate high solar power conversion efficiencies of 10% or more. Presumably the low performance of the former is partly because of the low probability of intermolecular electron transfer between the two components due to insufficient interface area or rapid charge recombination at the interface. In expectation of improved performance due to the high probability of intramolecular electron transfer, the fullerene-containing polymers **11**[35] and **12**[36] were recently presented (see Chart 5), giving well-behaved devices. Some fullerene-containing oligomers **13**,[37] **14**[38] and **15**[39] were also reported, but the efficiency of the device made from **13** was limited by competition of photoinduced electron transfer from the oligophenylene-vinylene moiety to the fullerene with efficient energy transfer. The discovery of highly efficient photoinduced electron transfer for the oligothiophene/fullerene dyad systems **3** not only in solution[13,14] but also in the solid state[40] prompted us to investigate their application to photovoltaic cells.[41]

A structure of Al/**3**/Au was fabricated, where the organic layer was prepared as a film by spin coating from chloroform solution (Fig. 5). In contrast to that of oligothiophenes **1**, the film of **3** showed no fluorescence, suggesting effective quenching due to electron transfer. Upon illumination from the Al side with a 10 μW cm^{-2} tungsten–halogen lamp attached to a monochrometer, a marked photocurrent was observed. On the other hand, similar illumination from the side of Au with a higher work function than Al generates only half of the current. These results suggest that most of carriers are generated at the interface between the Al metal and the organic layer and its neighborhood. The visible part of the action spectrum is in strict accordance with the absorption spectrum of the oligothiophene

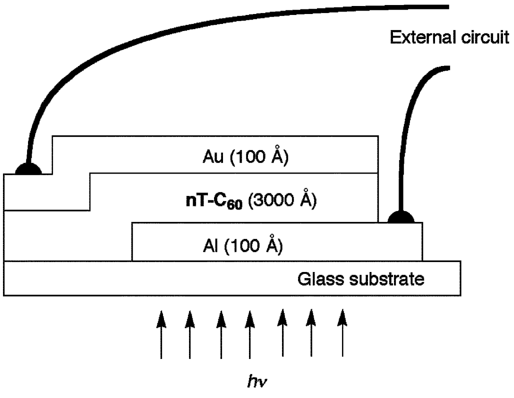
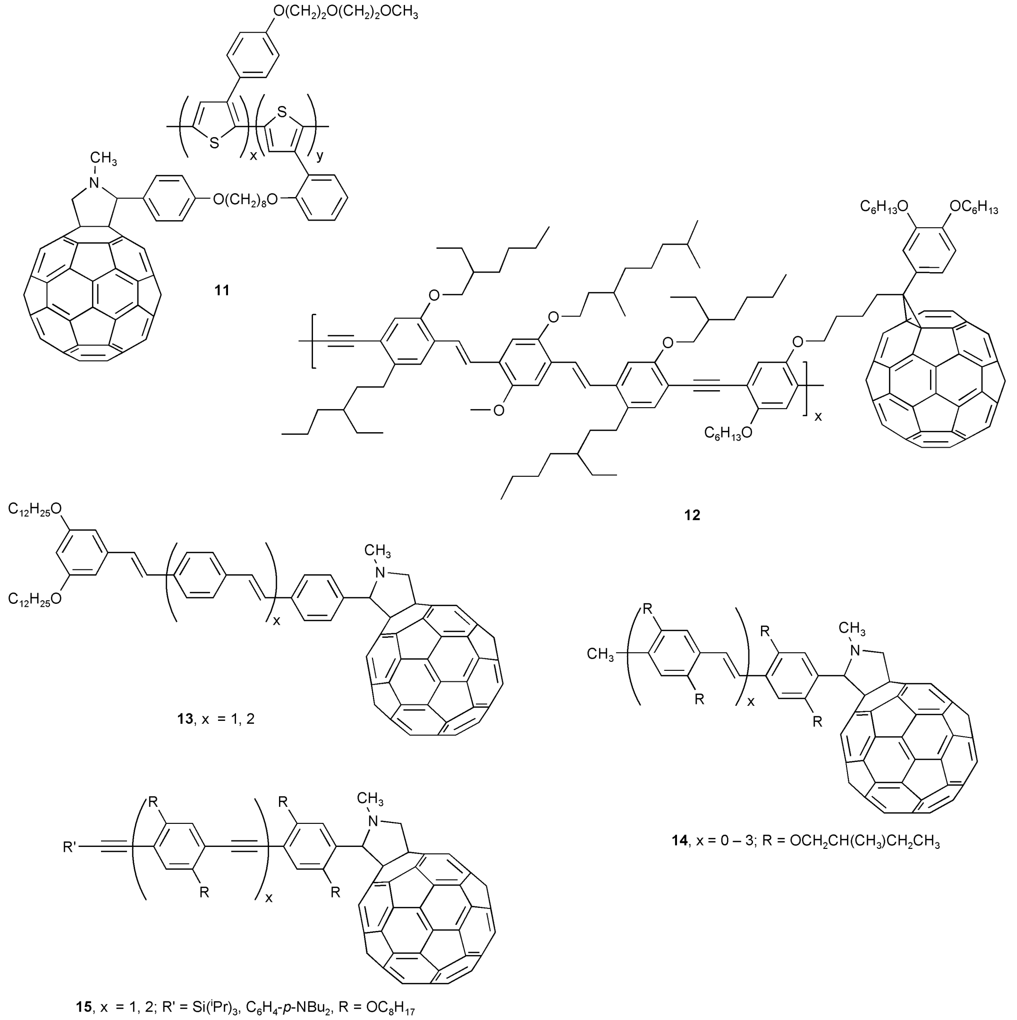


Fig. 5 Schematic structure of the *n*T-C_{60}-based photovoltaic cell.



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12

13, x = 1, 2

14, x = 0 – 3; R = $OCH_2CH(CH_3)CH_2CH_3$

15, x = 1, 2; R' = $Si(^iPr)_3$, C_6H_4-*p*-NBu_2, R = OC_8H_{17}

Chart 5 Fullerene-containing photoactive materials.

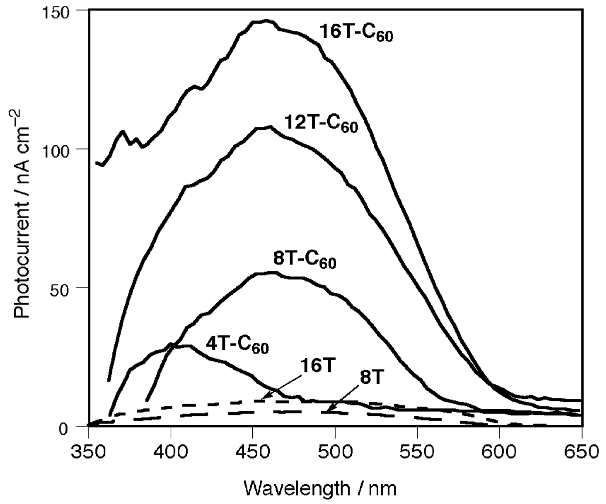
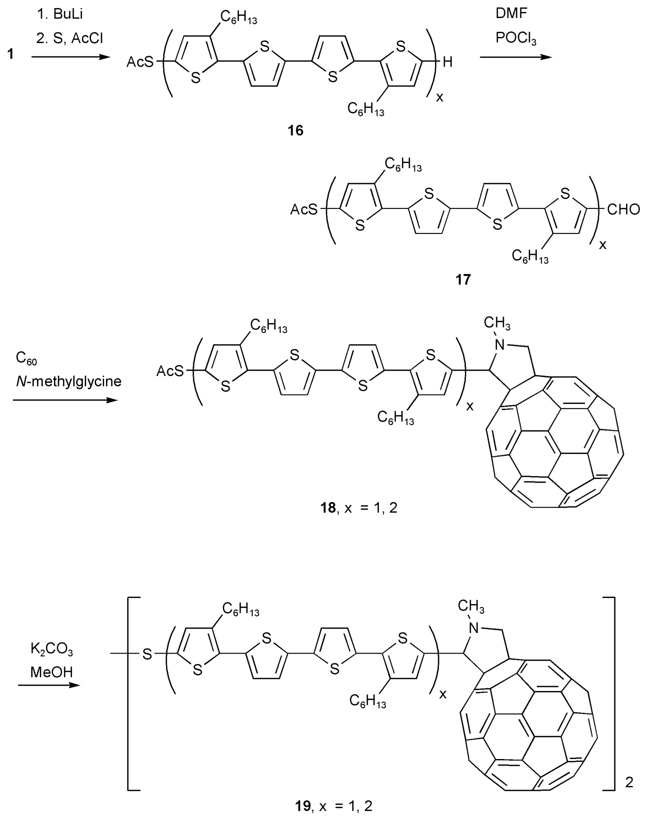


Fig. 6 Photocurrents of *n*T-C$_{60}$-based photovoltaic cells.

chromophore, and the short circuit current (I_{sc}) is markedly dependent on the oligothiophene length (Fig. 6). The generated photocurrent for each dyad is larger by one order of magnitude than that of the device using the unmodified oligothiophene **1**. It is thus evident that the intramolecular electron transfer of the dyad system contributes to the generation of photocurrent, becoming increasingly prominent with the chain extension of the oligothiophene. The incident photon converted to electron (IPCE) efficiency of these photovoltaic cells at maximum current is as follows: **4T-C$_{60}$**, 2.1%; **8T-C$_{60}$**, 3.7%; **12T-C$_{60}$**, 7.0%; **16T-C$_{60}$**, 9.7%. For the most effective **16T-C$_{60}$**, the conversion efficiency is evaluated to be 0.4%, which is reasonably high.



Scheme 3 Synthesis of the oligothiophene/fullerene system **19** containing a disulfide anchor.

5. Oligothiophene-containing SAM-based photovoltaic devices

Optoelectronic devices of photoactive molecules ordered on a metal electrode by a self-assembled monolayer (SAM) technique have received much current attention.[42] The unidirectional ordering of donor–acceptor molecules in the SAM provides an ideal system facilitating smooth electron flow, thus being applicable to the fabrication of highly efficient electronic devices including photovoltaic cells.[43] In this regard, we expected that a SAM containing the oligothiophene/fullerene dyad **3** would provide a better photovoltaic device than using the dyad in the bulk, described in Section 4. In order to implement this idea, we designed the fullerene-linked oligothiophene disulfides **19**, in which the disulfide anchoring group can be tethered onto a gold surface through an Au–thiolate interaction.[44] Since there had been a number of reports on thiophene-based SAMs,[45,46] **19** was also expected to make a highly ordered SAM. The synthesis of **19** was carried out using an acetylthio protecting group for the disulfide, as depicted in Scheme 3.

A SAM was prepared by immersion of the Au(111)/mica substrate in a saturated chloroform solution of **19**, and the amount of molecules adsorbed on Au was estimated from the charge of the first reduction peak of the fullerene moiety by a cyclic voltammetric experiment using the modified Au electrode (Fig. 7a). The different surface coverages of the quaterthiophene-containing molecule (3.5×10^{-11} mol cm^{-2}) and the

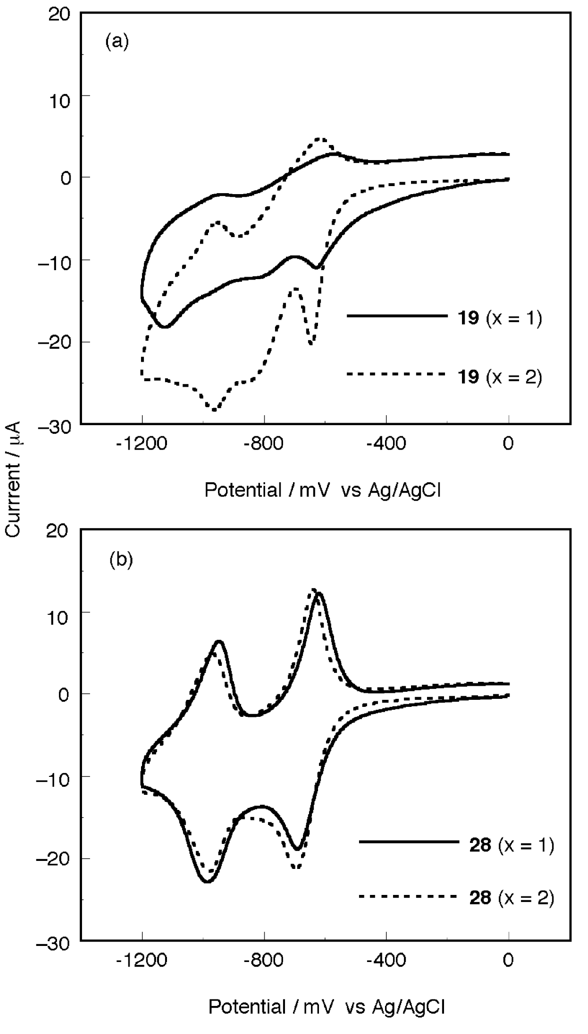


Fig. 7 Cyclic voltammograms of Au electrodes modified by the SAMs of (a) **19** and (b) **28**.

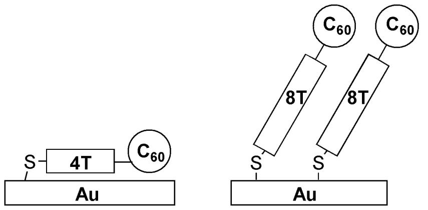
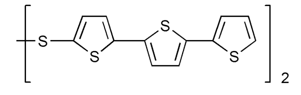


Fig. 8 Schematic drawing of SAMs comprising one-armed molecules.



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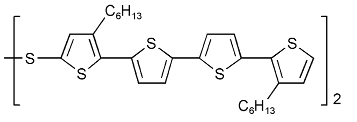

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Chart 6 SAM-forming oligothiophene disulfides.

octithiophene-containing molecule (8.9×10^{-11} mol cm^{-2}) were observed, suggesting that the former lies flat on the gold surface, while the latter stands proud (Fig. 8).

The difference between both structures probably arises from the different strengths of the molecular interactions. It is already known that the terthiophene disulfide **20** (Chart 6) can spontaneously assemble on a gold substrate,[46] and we have confirmed that this is also the case for the fullerene-free quaterthiophene disulfide **21** (Chart 6). In contrast, the small coverage for the fullerene-bearing quaterthiophene disulfide **19** ($x = 1$) indicates that the van der Waals interaction of the quaterthiophene is not strong enough to permit perpendicular alignment over the whole molecule. It is possible that both the fullerene and the sulfur atoms of the thiophenes interact with gold,[47] favoring horizontal alignment on the substrate. On the other hand, the large coverage for **19** ($x = 2$) indicates that the interaction of the octithiophene is strong enough to align perpendicularly over the molecule through aggregation. In addition, it may safely be said that the increase of the hexyl groups attached to the long oligothiophene is also favorable to strengthening the molecular interactions.

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 than that of the fullerene, and accordingly, the oligothiophene is the major absorber of visible photons. Under illumination of 440 nm light, the octithiophene-containing cell showed a marked photoelectrochemical response, as shown in Fig. 9. The cathodic photocurrent increases with an increase of the negative bias to the gold electrode (Fig. 10). This result clearly demonstrates that conduction electrons flow unidirectionally from the gold electrode to the counter electrode through the oligothiophene with a photoexcited function, as depicted in Fig. 11. The octithiophene-containing SAM provides a photoactive and charge-carrying building block useful for molecular-based electronics devices. On the other hand, the quaterthiophene-containing SAM scarcely responds to illumination. The lack of photocurrent for this device is ascribable to the molecular structure in the SAM, where the molecules adopt a horizontal alignment on the gold surface, resulting in quenching of the exciton state by gold.

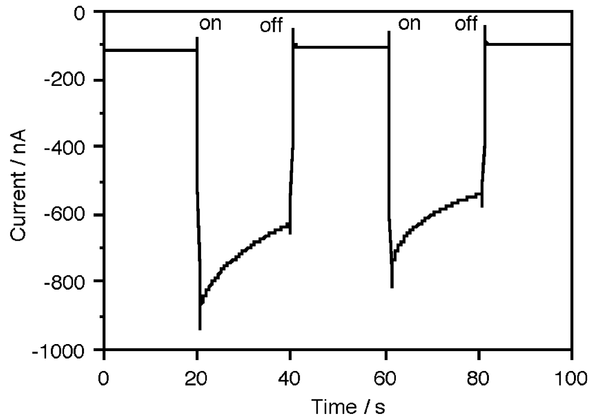


Fig. 9 Photocurrent response of the Au/**19** ($x = 2$)/MV^{2+}/Pt cell to 440 nm light.

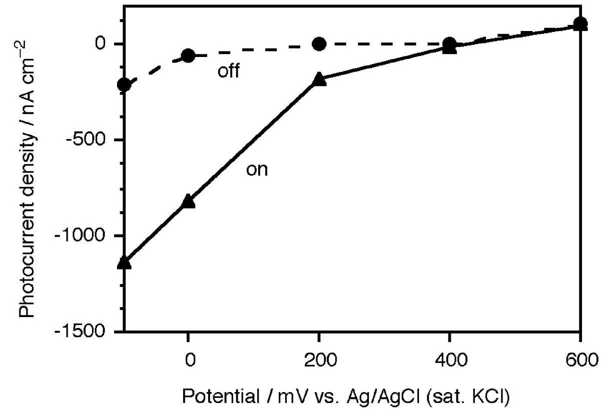


Fig. 10 Photocurrent *vs.* applied potential curves of the Au/**19** ($x = 2$)/MV^{2+}/Pt cell when the 440 nm light is on and off.

The above oligothiophene SAM-based photovoltaic results indicate that for the realization of high performance, it is important that the oligothiophenes be well-organized on the electrode. It should be noticed that the octithiophene-containing SAM with one-armed connection requires significant van der Waals interaction of the octithiophene for self-assembly, but such an interaction is more of a disadvantage for the generation of a photocurrent because it must quench the initial photoexciton state. It is thus desirable to use a molecule which

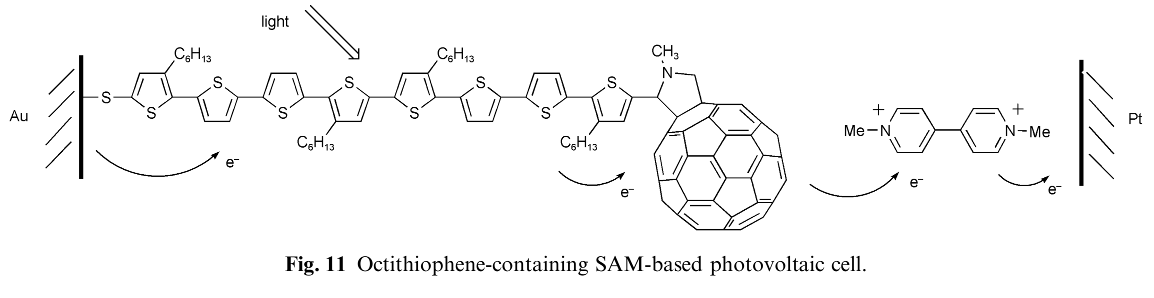
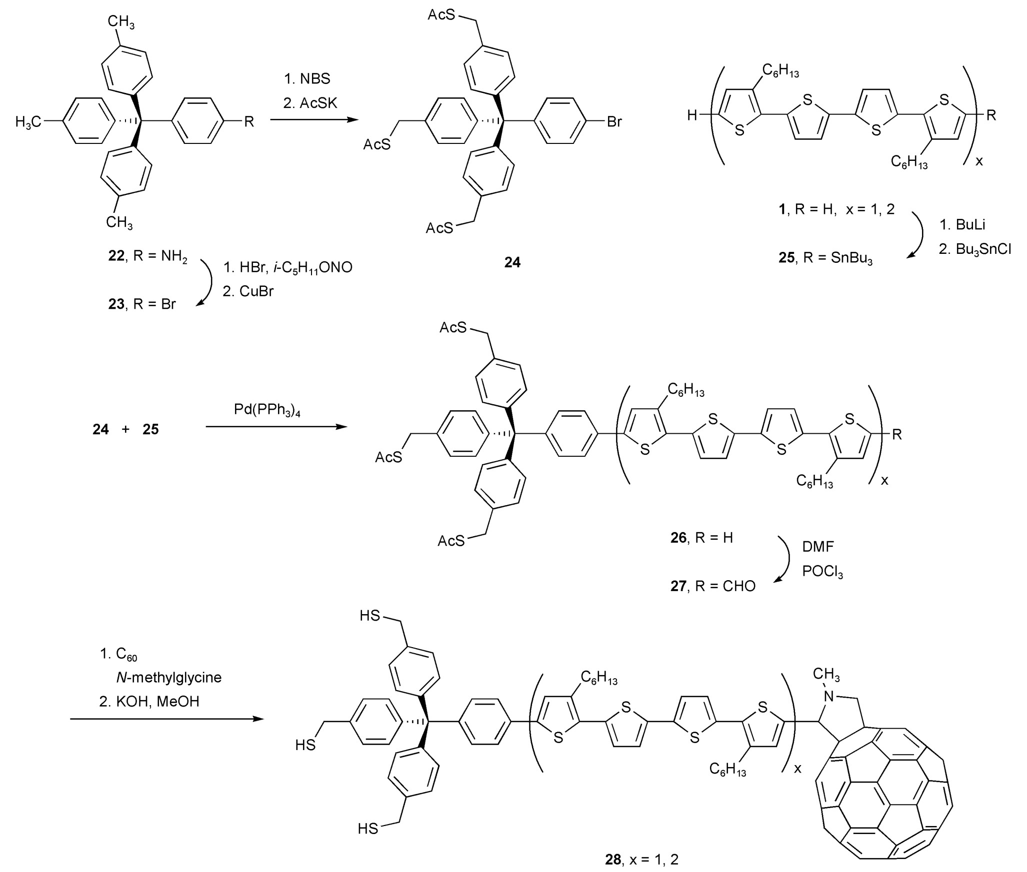


Fig. 11 Octithiophene-containing SAM-based photovoltaic cell.



Scheme 4 Synthesis of the tripodal anchoring oligothiophene/fullerene system **28**.

self aligns perpendicularly to the surface with no intermolecular interaction in the SAM. For this purpose, a protocol using a three-armed anchor for SAM formation has been recently proposed.[48] In this respect, we synthesized the oligothiophene/fullerene system **28** bearing a tripodal rigid anchor, which is a tetraphenylmethane core with three mercaptomethyl arms, as shown in Scheme 4.[49] The tripodal anchor is expected to ensure vertical or perpendicular alignment on the gold surface.

In contrast to the irreversible redox waves of **19**/Au, the tripodal **28**/Au exhibited well-defined redox waves (Fig. 7b), indicating that the molecules are strongly adsorbed on the surface due to three-armed connection. From the surface coverages of the quaterthiophene-containing molecule (1.7×10^{-10} mol cm^{-2}) and the octithiophene-containing molecule (1.6×10^{-10} mol cm^{-2}), it can be understood that the tripodal molecules (**28**) are more densely adsorbed than the one-armed molecules (**19**). In addition, the amounts of the two three-armed molecules adsorbed are virtually the same, independent of the oligothiophene length. Considering their symmetry, the three-armed molecules stand by themselves perpendicular to the gold surface, as illustrated in Fig. 12.

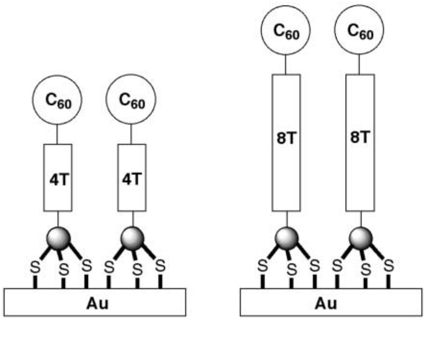
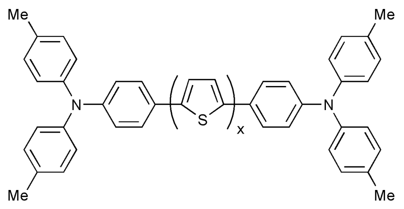


Fig. 12 Schematic drawing of SAMs comprising three-armed molecules.

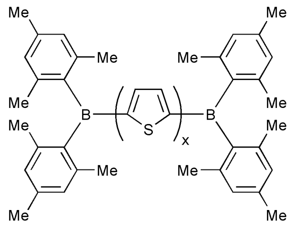
The magnitudes of the photocurrents generated using the **28**/Au electrodes are remarkable amongst SAM-based photovoltaic cells. The photocurrent density of the Au/**28** ($x = 1$)/MV^{2+}/Pt cell is much larger, by a factor of about 190, than that observed for the Au/**19** ($x = 1$)/MV^{2+}/Pt cell. The photocurrent of the Au/**28** ($x = 2$)/MV^{2+}/Pt cell is about six times larger than that of the Au/**19** ($x = 2$)/MV^{2+}/Pt cell. The enhanced photoresponse is primarily attributable to the more densely packed SAMs, but the enhancement ratio of the photocurrents for the two octithiophene-containing cells greatly exceeds the increased ratio (1.6 times) of the surface coverages. As expected, the quenching of the photoexcited state by intermolecular interactions must be depressed. In addition, it may be considered that the terminal tetraphenylmethyl core contributes to block a reverse electron flow from the oligothiophene to the Au electrode. The quantum yields based on the number of absorbed photons are 17% for the Au/**28** ($x = 1$)/MV^{2+}/Pt cell and 35% for the Au/**28** ($x = 2$)/MV^{2+}/Pt cell. Evidently the long oligothiophene chain can facilitate the generation of photocurrent, and is reminiscent of the case seen for the above photovoltaic devices using the bulk films of oligothiophene/fullerene dyads **3**.

6. Oligothiophene-based EL devices

Oligothiophenes have been successfully used as active components in organic electroluminescence (EL) devices.[4a] The EL performances of single-layer devices using simple oligothiophenes are, however, generally low,[50,51] so multi-layered devices have been fabricated for the improvement of EL performance.[52] Structural modifications of oligothiophenes themselves have offered another approach to attain high efficiency. Shirota and co-workers demonstrated that oligothiophenes modified with electron-donating bis(4-methoxyphenyl)aminophenyl units and with electron-withdrawing dimesitylboryl units gave superior



29, x = 1 – 4

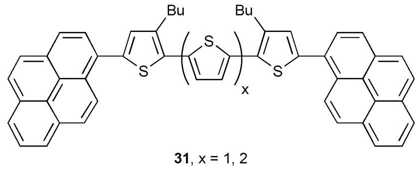


30, x = 2, 3

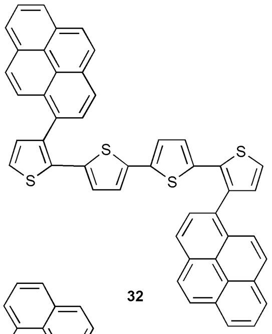
Chart 7 Oligothiophene-based light emitting materials.

hole-transporting materials (**29**, Chart 7)[53] and electron-transporting materials (**30**, Chart 7),[54] respectively, which were successfully used in multi-layer EL devices. In the devices, compounds **29** are also useful as light-emitting materials, whose emission wavelengths are tunable *via* the oligothiophene lengths.

For the purpose of the improvement of the emission properties, we investigated oligothiophenes **31**–**33** (Chart 8) modified with fluorescent pyrenes at the α- or β-positions.[55] The introduction of pyrenes has the advantages of not only enhancing the fluorescence but also the thermal stability and charge-transport capability of the oligothiophene films. The synthesis of these compounds was carried out using transition metal-catalyzed aryl–aryl coupling reactions such as the Kumada,[56] Stille[57] or Suzuki couplings,[58] as exemplified for the synthesis of **31** in Scheme 5.



31, x = 1, 2



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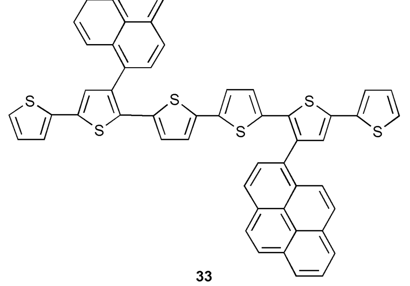

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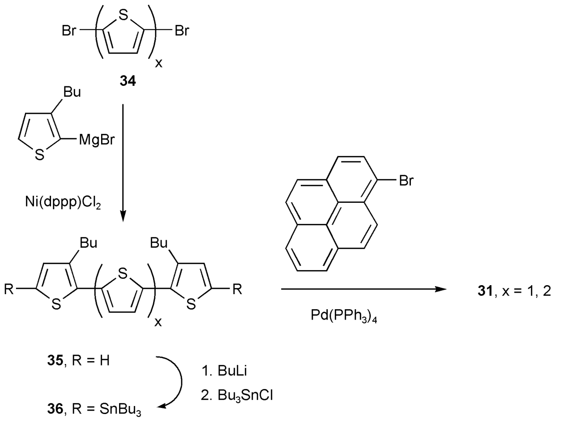
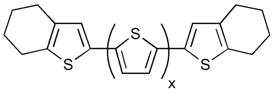
Chart 8 Pyrene-bearing oligothiophenes.



Scheme 5 Synthesis of pyrene-bearing oligothiophenes **31**.

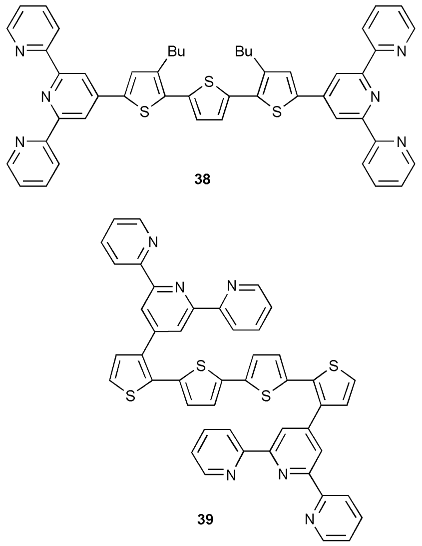
The single-layer EL devices of the pyrene-bearing oligothiophenes sandwiched between an ITO electrode and an Al/LiF bilayer electrode emitted versatile visible light depending on the chain lengths and the substitution positions (**31**, $x = 1$, yellow; **31**, $x = 2$, orange; **32**, green; **33**, orange; Chart 8), and the EL spectra have close resemblance to the respective PL spectra. The maximum brightness of these EL devices except for that of **31** ($x = 1$) is however rather low despite the high current density: **31** ($x = 1$), 1860 cd m^{-2} at a driving voltage of 12.5 V; **31** ($x = 2$), 53 cd m^{-2} at 13.7 V; **32**, 130 cd m^{-2} at 9.5 V; **33**, 37 cd m^{-2} at 14.5 V. Comparisons of these devices in the respective α- and β-substitution series evidently indicate that the EL performance tends to decrease with increasing chain lengths of oligothiophenes, being reminiscent of that found for the preceding devices based on end-capped oligothiophenes **37** (Chart 9).[50] The low brightness of the EL devices is understandable in terms of the inherent p-type semiconducting characters of oligothiophenes, which favor hole injection from the anode more effectively than electron injection from the cathode. The chain extension of the oligothiophene backbone probably strengthens the p-type character much more to promote a charge unbalance in the single-layer structure. Consistent with this explanation, the maximum luminance of the pyrene-bearing oligothiophenes can be enhanced by one order of magnitude by the fabrication of double-layer structures, where 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) is incorporated as a hole-blocking layer.

The p-type characteristics of the pyrene-bearing oligothiophenes prompted us to study the terpyridine-bearing oligothiophenes **38** and **39** (Chart 10) for EL materials.[59] We expected that the incorporation of the electron-deficient terpyridine groups would serve to introduce an amphoteric ability into an oligothiophene. Both single-layer EL devices, using **38** or **39**, emit green light and show better performance because of an improved balance between injected holes and electrons, when compared to the devices based on the above pyrene-bearing oligothiophenes. In particular, it is worth noting that the device ITO/**39**/LiF/Al turns on at 5.5 V and exhibits a maximum luminance of 2950 cd m^{-2} at a driving voltage of 11.5 V and a maximum luminous efficiency of 0.22 lm W^{-1} (Fig. 13). This is a good performance for a single-layer EL device. These terpyridine-bearing oligothiophenes, however, assume characteristics of an electron-transport type. Thus the double layer EL device ITO/TPD/**39**/LiF/Al, fabricated in combination with



37, x = 2 – 5

Chart 9 End-capped oligothiophenes.



38

39

Chart 10 Terpyridine-bearing oligothiophenes.

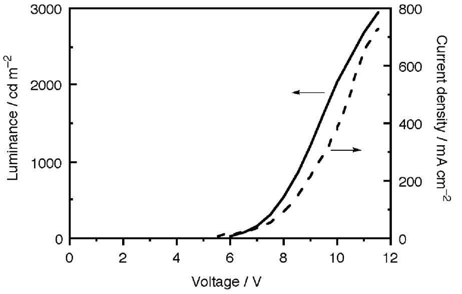
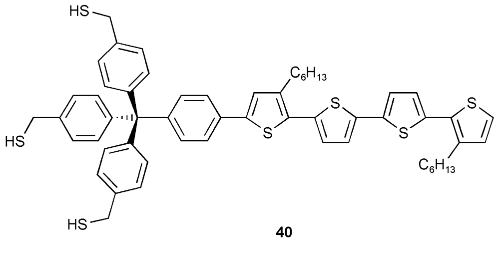


Fig. 13 Voltage *vs.* luminance and current density curves of the ITO/**39**/LiF/Al device.

a typical hole-transport material *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD), exhibits a remarkable maximum luminance of 10830 cd m^{-2} at a driving voltage of 18.4 V.

The Au electrode modified with oligothiophene containing SAM also has the advantage of application to EL devices.[60] For this study, we used the tripod-shaped molecule **40** (Chart 11), since the three-armed anchor can form a stable SAM, as already stated. Compound **40** was prepared by hydrolysis of the preceding intermediate **26** ($x = 1$) and adsorbed on an Au/mica substrate. When installed in an EL device, the oligothiophene containing SAM is expected to facilitate hole injection from the electrode to the organic layer. This is actually the case for the Mg–Ag/Alq$_3$/TPD/**40**-SAM/Au device [Fig. 14, Alq$_3$ = tris(8-quinolinolato)aluminium(III), an emitter];[61] its luminescence–voltage characteristic is shifted considerably to the low voltage direction, as compared to the similar device without the SAM. For example, the turn-on voltage decreases from 7 to 4 V. This large reduction in the operating voltage is possibly related to high organization of oligothiophenes, increasing adhesion between the SAM and TPD layers and markedly promoting charge transfer through the oligothiophene spacer from the Au anode to the TPD layer.



40

Chart 11 Tripod anchoring quaterthiophene.

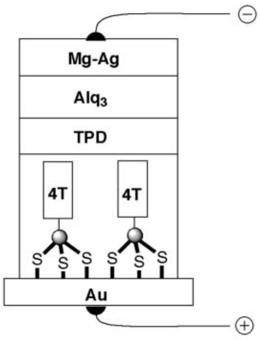


Fig. 14 Illustration of the Mg–Ag/Alq$_3$/TPD/**40**-SAM/Au device.

7. Concluding remarks

Oligothiophenes have many advantages in accessibility, structural modification, solubility, rigidity and stability, and accordingly are promising materials to meet requirements for molecular devices. We have demonstrated here some concrete examples that oligothiophenes can be appropriately modified with electro- or photo-active chromophores such as fullerenes, porphyrins, pyrenes and terpyridines, and the resulting functional oligothiophenes can be successfully applied to the fabrication of photovoltaic cells and EL devices. In addition, it has turned out that a highly conjugated oligothiophene inserted between a donor and an acceptor has a high capability as a long-range electron transfer wire. One important interest in such functional oligothiophenes is their possibility for use as molecular kits for nanoarchitectures. To date, synthetic strategies for long oligothiophenes with lengths suitable for nanoelectrode spanning have been well established. However, the delicate nanofabrication needed to attach such a molecular wire to a nanoelectrode is still problematic. A SAM technique offers a possibility of attachment, that is, functional oligothiophenes bearing a thiol or disulfide anchoring group can be conveniently tethered on a gold surface by an Au–thiolate interaction. In particular, it is worth noting that use of a tripodal anchoring group ensures vertical (perpendicular) alignment on the gold surface and this is very important for the formation of a stable, dense SAM. The oligothiophene-containing SAMs thus obtained are very usable as a photoactive and charge-carrying building block in highly efficient photovoltaic devices. We expect that further research on functional oligothiophenes will promote a basic understanding of nanomolecules and their applications to molecular electronic devices.

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