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Jotaro Nakazaki,[1] InGwon Chung,[1] Ryoji Watanabe,[2] Toshiyuki Ishitsuka,[2] Yuzo Kawada,[2] Michio M. Matsushita,[1] and Tadashi Sugawara[1]

[1] Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153–8902, Japan
[2] Department of Materials and Biological Sciences, Faculty of Science, Ibaraki University, Bunkyo, Mito, Ibaraki 310–8512, Japan

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Design of Spin–Polarized Molecular Wire as a Prototypal Unimolecular Quantum Spin Device[#]

Jotaro Nakazaki,[1] InGwon Chung,[1] Ryoji Watanabe,[2] Toshiyuki Ishitsuka,[2] Yuzo Kawada,[2] Michio M. Matsushita,[1] and Tadashi Sugawara[1],*

[1] Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153–8902, Japan
[2] Department of Materials and Biological Sciences, Faculty of Science, Ibaraki University, Bunkyo, Mito, Ibaraki 310–8512, Japan

Abstract
Motivation. Development of a series of "spin–polarized donors", which afford ground state triplet cation diradicals upon one–electron oxidation, promoted us to produce a hyper–structured spin–polarized donor, because it can be regarded as a unimolecular quantum spin device if it is equipped with conducting wires and terminals to access to electrodes.
Results. A pyrrole–based spin–polarized donor carrying oligothiophene molecular wires has been prepared. The magnetic coupling along the oligothiophene wire turned out to be effective as far as the number of monomer units does not exceed six.
Conclusions. The spin–polarized molecular wire, which consists of a spin–polarized donor core, molecular wires, and terminals, is expected to operate as a spin–rectifier, demonstrating spin–polarized Coulomb oscillations.
Keywords. Unimolecular device; spin–polarized donor; oligomer; ESR.

1 INTRODUCTION

Various functions of organic materials, such as conductivity, magnetism, non–linear optics, *etc*., are derived from the characteristic π–electronic structure. Whereas long linear π–conjugated systems exhibit an electrical conductivity upon doping, arrangement of sp^2 carbons in a cross–conjugated manner affords a branched π–system exhibiting magnetism due to the intrinsic appearance of unpaired electrons. Thus, it can be said that nature of a π–conjugated systems depends largely on its topology. Taking account of such a topological nature of π–systems, several high spin molecules have been created and significance of these high spin molecules as one–

[#] Dedicated to Professor Haruo Hosoya on the occasion of the 65th birthday.
* Correspondence author; fax: +81–3–5454–6997; E–mail: suga@pentacle.c.u–tokyo.ac.jp.

dimensional ferromagnets has been documented [1–3]. Nowadays extremely high spin molecules of which spin quantum number exceeds 40 have been constructed [4].

Recently, novel high spin species, which is derived from so–called "spin–polarized donor", has been proposed [5–10]. A spin–polarized donor consists of a donor and radical units, and these units are connected in a cross–conjugating manner. Although unpaired electrons of a spin–polarized polyradical donor behave independently in the neutral state, they communicate each other when a π–cation radical is generated upon single–electron oxidation, namely the spin correlation between unpaired electrons residing non–degenerated SOMOs is achieved [7]. Such transformation of spin states can be utilized as a switching function of a spin electronic device.

Many material physicists are now devoted themselves into quantum devices [11]. Recent progress in constructing a quantum well or a quantum dot made of semiconductors, such as gallium–arsenide, for example, enables to decrease the size of diameters less than 200 nm. When the size becomes that small, its electronic structure becomes quantized to have discrete energy levels just like those of a molecule. It is also found that an orbital–filling with electrons in the quantum dot obeys Hund's rule [12]. Accordingly, such a quantum dot can be regarded as a superatom. If the dots are located closely enough to be electronically communicative, an array of quantum dots may be regarded as a supermolecule. People now are much interested in the spin–dependent phenomenon observed in these quantum structures [13–15].

Since such a quantized electronic structure is an intrinsic feature of organic molecules, they can be regarded as ultimate quantum dots. In order to make them operate as molecular devices, the size of the functional molecule should be reasonably large to be accessed by an external detecting system. Recent progress in organic synthesis enables us to prepare π–conjugated giant molecules with a length longer than 5 nm [16–19]. Such long π–conjugated molecules are called "molecular wires". If a spin–polarized molecular wire is synthesized, it will work as a unimolecular quantum spin device.

2 RESULTS AND DISCUSSION

2.1 Spin–Polarized Donor as a Core of a Quantum Spin Device

When a spin–polarized donor is singly oxidized, it affords a ground state triplet cation diradical. The characteristics in the electronic structure of the spin–polarized donor is shown in Figure 1. In the case of an ordinal organic π–radical, the unpaired electron in SOMO is removed upon one–electron oxidation as shown in Figure 1(*a*). On the other hand, a spin–polarized donor affords a ground state triplet cation diradical upon one–electron oxidation (Figure 1(*b*)) since the orbital energy level of NHOMO(β) is higher than that of SOMO(α). The electronic structure of the spin–polarized donor is advantageous to construct a spin–polarized core unit of a quantum spin–

electronic device.
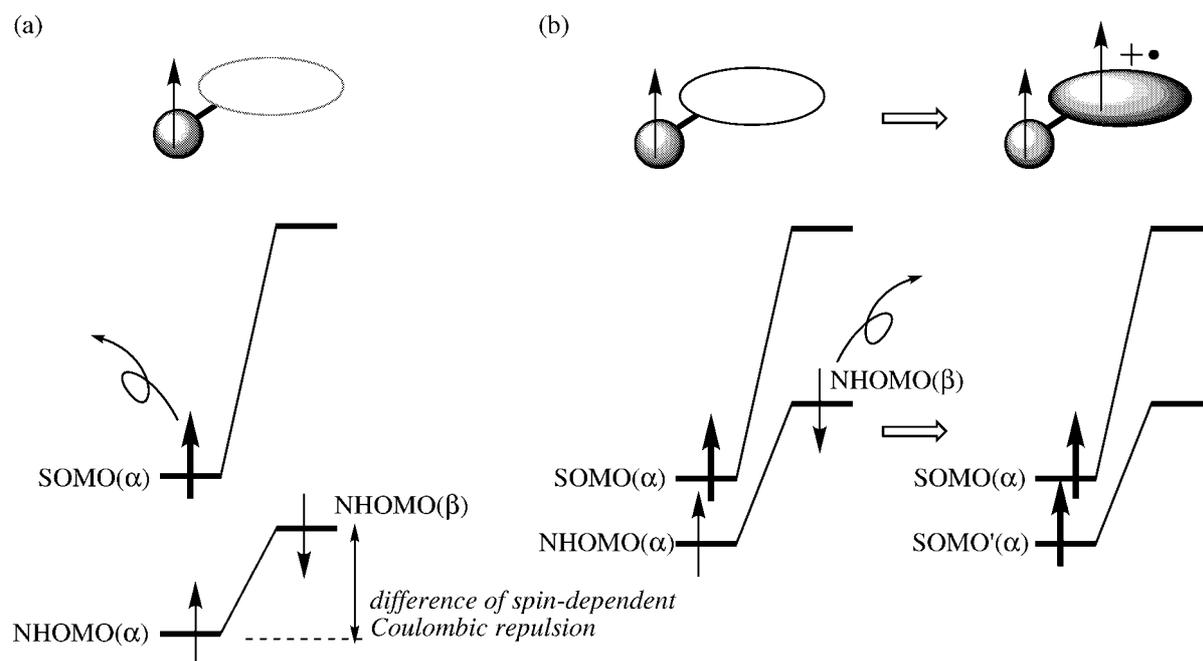
Figure 1. Schematic drawings of the electronic structures of (*a*) an ordinal organic radical and (*b*) a spin–polarized donor. SOMO: singly occupied molecular orbital; NHOMO: next highest occupied molecular orbital; SOMO': SOMO derived from NHOMO upon one-electron oxidation

2.1.1 Topological control of high spin state of biradicals

When two organic π–radicals are connected directly at their "active" sites, where unpaired electrons reside, the connection leads to a π–conjugated molecule without unpaired electrons. If two radical units are connected at their "inactive" sites, the resulted diradical is classified as a "disjoint" type [20]; Tetramethyleneethane (TME: **1**) is a diradical of this type. The exchange interaction in such disjoint diradicals is negligibly small and they exist as ground state singlet species. On the other hand, a "non–disjoint" diradical is formed by connecting two radical units at an "inactive" and an "active" sites. Trimethylenemethane (TMM: **2**), which is composed of an allyl radical and a methyl radical, is classified as this type of diradical with the triplet ground state spin multiplicity.
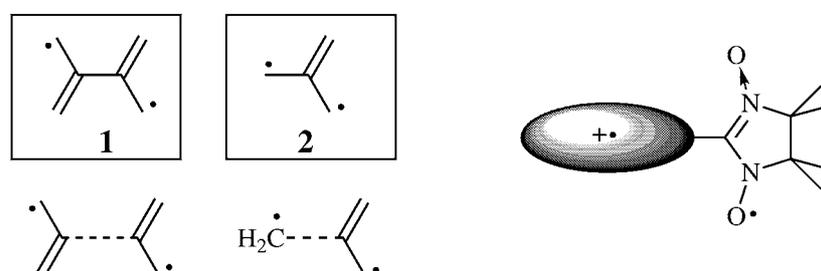

Figure 2. A nitronyl nitroxide derivative connected with a cation radical of a donor molecule.

A nitronyl nitroxide is regarded as a hetero–analogue of an allyl radical, in which terminal carbons are replaced with N–O groups. Accordingly, a "non–disjoint" type connectivity is achieved

if the nitronyl nitroxide is introduced at an "active" site of a cation radical of a donor unit (Figure 2). Since SOMO' of a cation radical of the donor unit is derived from its HOMO, most positions of the donor unit are "active" sites.

2.1.2 Pyrrole–based spin–polarized donors

Spin–polarized donors so far reported are amine–, thianthrene–, tetrathiafulvalene (TTF)–, and pyrrole–based derivatives [5–10]. Among them, a pyrrole–based spin–polarized donor is appropriate as a building block of molecular wires because it is readily extended to π–conjugated oligomers and polymers. The above background has promoted us to prepare a series of pyrrolyl nitronyl nitroxide derivatives [10]. Whereas the ground state spin multiplicity of the cation diradical of 1–pyrrolylNN (**3**) is singlet, a *p*–phenylene–extended derivative **4** turns out to afford a ground state triplet species upon one–electron oxidation. Since this donor–radical **4** is free from the regioregularity problem, it is an appropriate candidate of a core unit of the spin–polarized molecular wire.

3   **4**
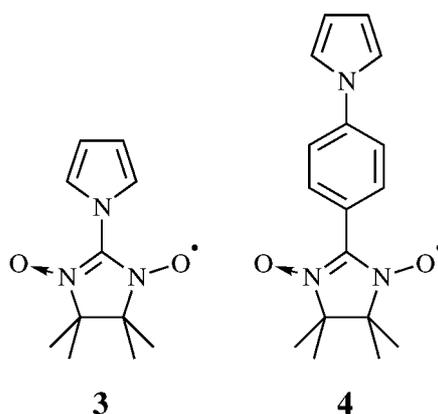
2.2 Spin–Polarized Donor Equipped with Molecular Wire

As described above, a spin–polarized donor tends to donate a β–spin electron, provided that the spin of an unpaired electron is α. If a molecular wire, such as an oligothiophene, is connected to the suitable position of the spin–polarized donor core, only a β–spin electron can pass through the molecular wire, a spin–polarized donor operating as a spin aligner. A schematic drawing of this idea is depicted in Figure 3.

According to the above idea, 1–pyrrolylphenylNN bearing oligothiophenes at 2– and 5–positions has been designed. There are, however, two problems to be considered seriously. First, since the extension of the π–system decreases the magnitude of the coefficients of the partial HOMO of the donor unit, it may diminish the non–disjoint character. Second, twisting of the thienyl and/or the phenyl rings from the plane of the pyrrole ring may break the π–conjugation of these parts. In order to examine these factors, thiophene–pyrrole hybrid trimer **5** and oligomer **6** were prepared.
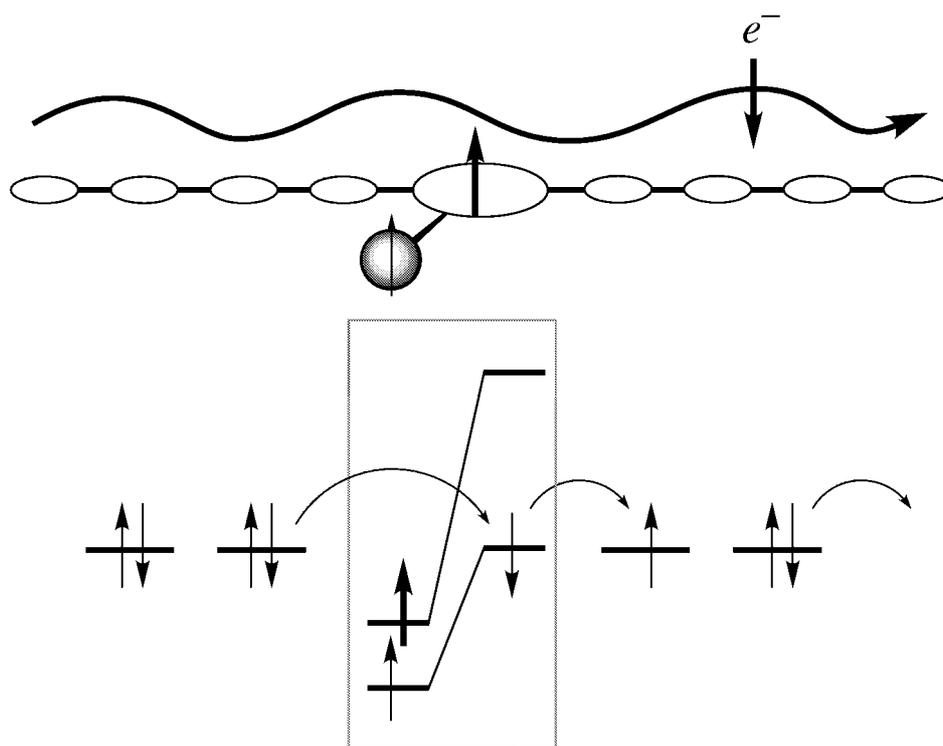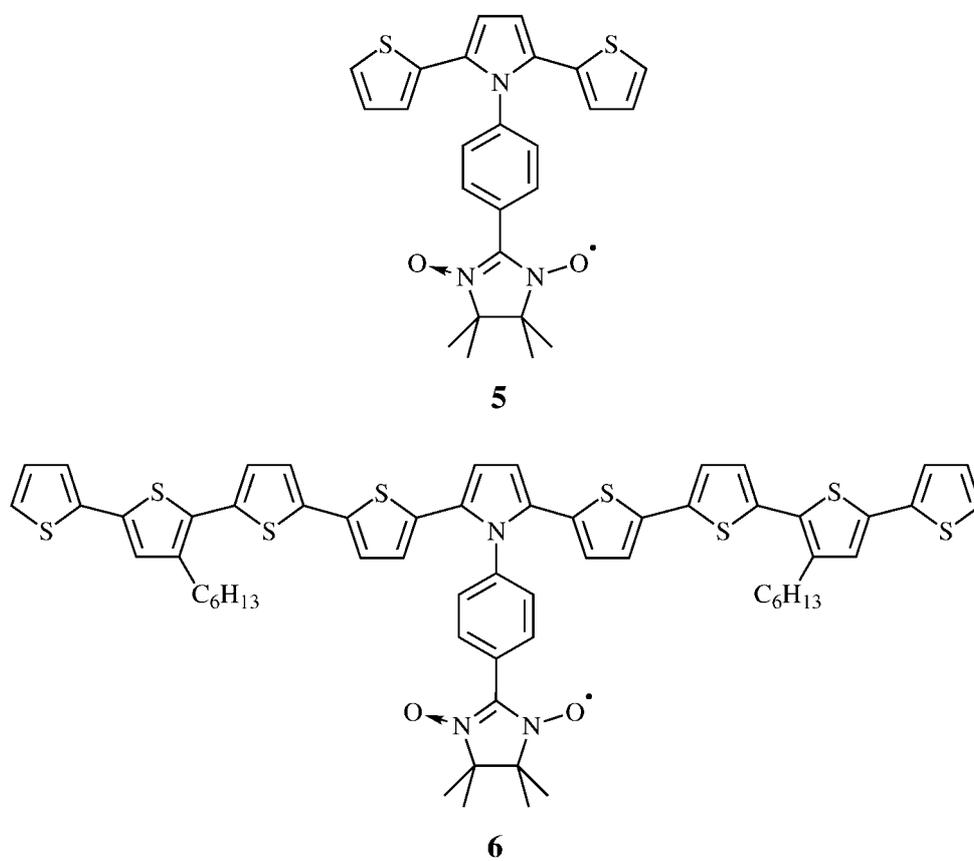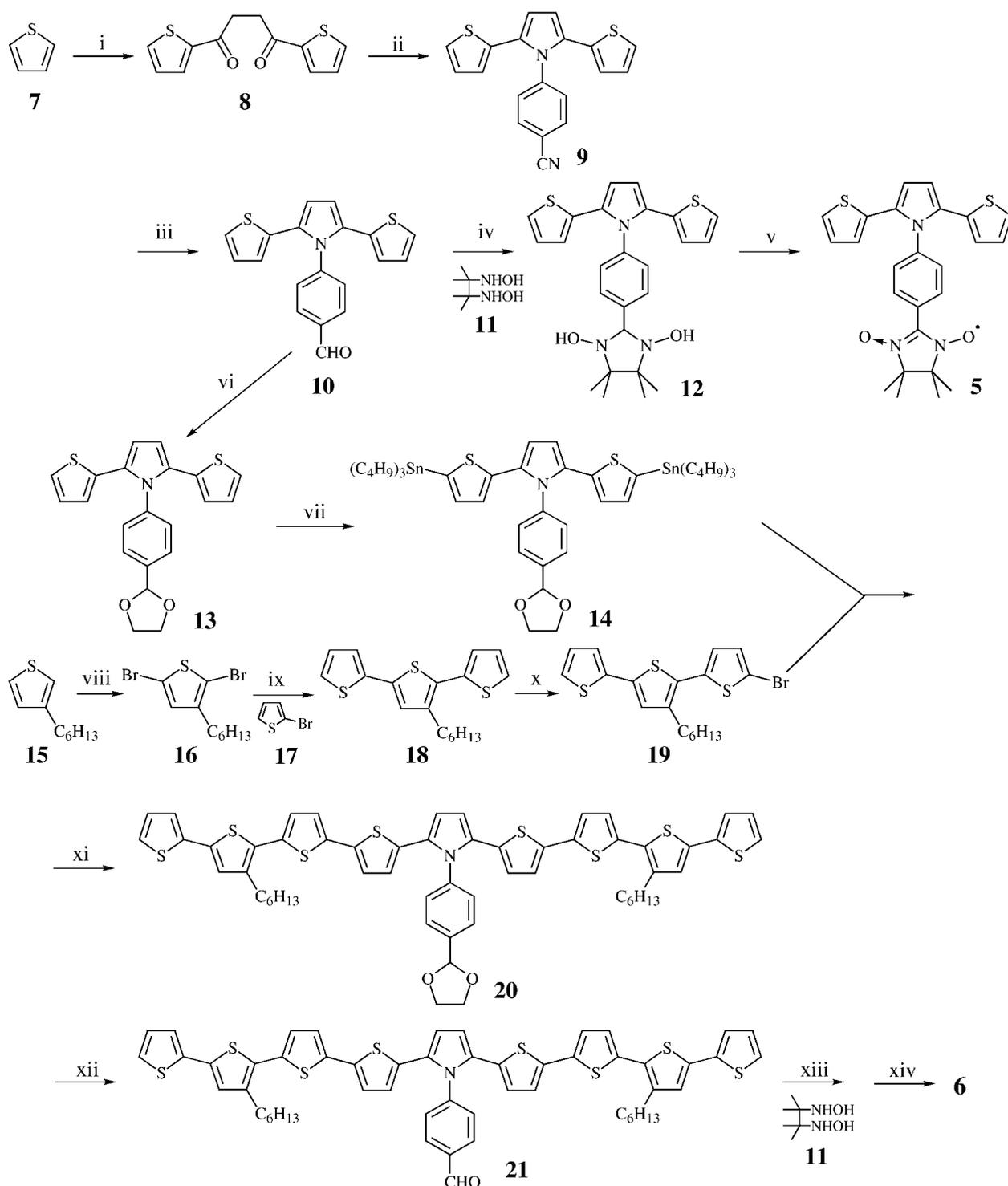
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Figure 3. Schematic drawing of the concept of spin–rectification.

5

6

Figure 4. Synthetic scheme of the preparation of thiophene–pyrrole hybrid oligomer type donor–radical. Reagents and conditions: (i) (CH₂COCl)₂, AlCl₃, CH₂Cl₂, 15°C, 4 h, 55 %; (ii) *p*–(NH₂)C₆H₄CN, *p*–TsOH•H₂O, xylene, reflux, 12 h, 80 %; (iii) 1) *i*–Bu₂AlH, PhCH₃, –60°C, 1 h, 2) HCl *aq*., r.t., 3 h, 95 %; (iv) **11**, **11**•H₂SO₄, PhH–MeOH, reflux, 8 h, 75 %; (v) PbO₂, K₂CO₃, THF, r.t., 2 h, 45 %; (vi) (CH₂OH)₂, *p*–TsOH•H₂O, PhH, reflux, 10 h, quant.; (vii) 1) LDA, THF, –78°C to –50°C, 2 h, 2) *n*–Bu₃SnCl, THF, –78°C to r.t., 3 h, 80 %; (viii) NBS, DMF, 40°C, 4 h, 85 %; (ix) **17**–Mg, Ni(dppp)Cl₂, Et₂O, reflux, 2 h, 55 %; (x) NBS, DMF, –60°C to r.t, 12 h; (xi) Pd(PPh₃)₄, PhCH₃, 80°C, 36 h, 60 %; (xii) *p*–TsOH•H₂O, CHCl₃–acetone, r.t., 10 h, quant.; (xiii) **11**, **11**•H₂SO₄, PhH–MeOH, reflux, 8 h, 40 %; (xiv) PbO₂, K₂CO₃, PhH, r.t., 30 min, 70 %.

2.2.1 Preparation of donor radials of a thiophene–pyrrole hybrid oligomer type

Preparative routes of thiophene–pyrrole hybrid trimer **5** and oligomer **6** are shown in Figure 4. Friedel–Crafts acylation of thiophene (**7**) with succinyl chloride, followed by a dehydrative cyclization of diketone **8** with *p*–aminobenzonitrile, gave rise to 2,5–bis(2–thienyl)–1–(*p*–cyanophenyl)pyrrole (**9**), which was converted to aldehyde **10**. Treatment of aldehyde **10** with bishydroxylamine **11**, followed by PbO_2 oxidation, afforded nitronyl nitroxide **5**. In order to obtain thiophene–pyrrole hybrid nonamer, aldehyde **10** was converted to acetal **13**, which was lithiated, stannylated, and coupled with terthiophene bromide **19** using a palladium(0) catalyst. The bromide **19** was obtained by bromination of terthiophene **18** with *N*–bromosuccinimide in dimethylformamide at room temperature, as a mixture of 3'–hexyl and 4'–hexyl derivatives with a ratio of *ca*. 20:1. The resulted nonamer–acetal **20** was converted to aldehyde **21**, which was treated with bishydroxylamine **11**, followed by PbO_2 oxidation, to afford the nitronyl nitroxide **6**. FAB–HRMS of **6** was m/z = 1122.2449 (calcd. 1122.2451 for $C_{61}H_{60}N_3O_2S_8$).

2.2.2 Electronic interaction between spin–polarized core and molecular wire

The cyclic voltammogram of oligomer **6** showed reversible oxidation waves at +0.63 and +0.78 V (vs. Ag/AgCl, in 0.1M *n*–Bu₄NClO₄/PhCN). When potentials higher than 1.0 V were applied, polymerization of oligomer **6** was observed. The first oxidation potential of oligomer **6** (+0.63 V) is lower than those of trimer **5** (+0.68 V) and monomer **4** (+0.80 V), suggesting that the π–extension of the oligomer caused a reasonable improvement of the donor ability.

This tendency is also supported by the red–shifted absorption maximum of oligomer **6** at 438 nm (Figure 5). Referring to the absorption maxima of sexithiophene (T6) at 413 nm, T13 at 453 nm, T20 and T26 at 461 nm reported by Otsubo *et al*. [18], the absorption maximum of oligomer **6** turns out to lie between those of T6 and T13. Accordingly, the effective π–conjugation in oligomer **6** is achieved as a molecular wire in spite of a congested environment around the 2,5–bis(α–thienyl)–*N*–phenylpyrrole unit.

When oligomer **6** was oxidized with iodine, a set of multiplet ESR signals were observed together with a broad signal at the region of *g* = 2 at low temperatures. Since the multiplet signal is in accord with that of the cation diradical of trimer **5** ($D = 0.0259$ cm^{-1}, $E = 0.0020$ cm^{-1} [10]), they can be assigned to the triplet species of oligomer **6**$^{+•}$. The central broad signal may be derived from the aggregated high spin species of **6**$^{+•}$. Therefore, it is concluded that the delocalizing π–spin generated by the oxidation of **6** is coupled ferromagnetically with the local spin on the radical site.

These experimental results indicated that the aforementioned problems are not critical in the current case: The π–conjugation of the thiophene–pyrrole chain is maintained in spite of the congested environment around the pyrrole ring, leading to the ground state triplet spin multiplicity of the singly oxidized species.
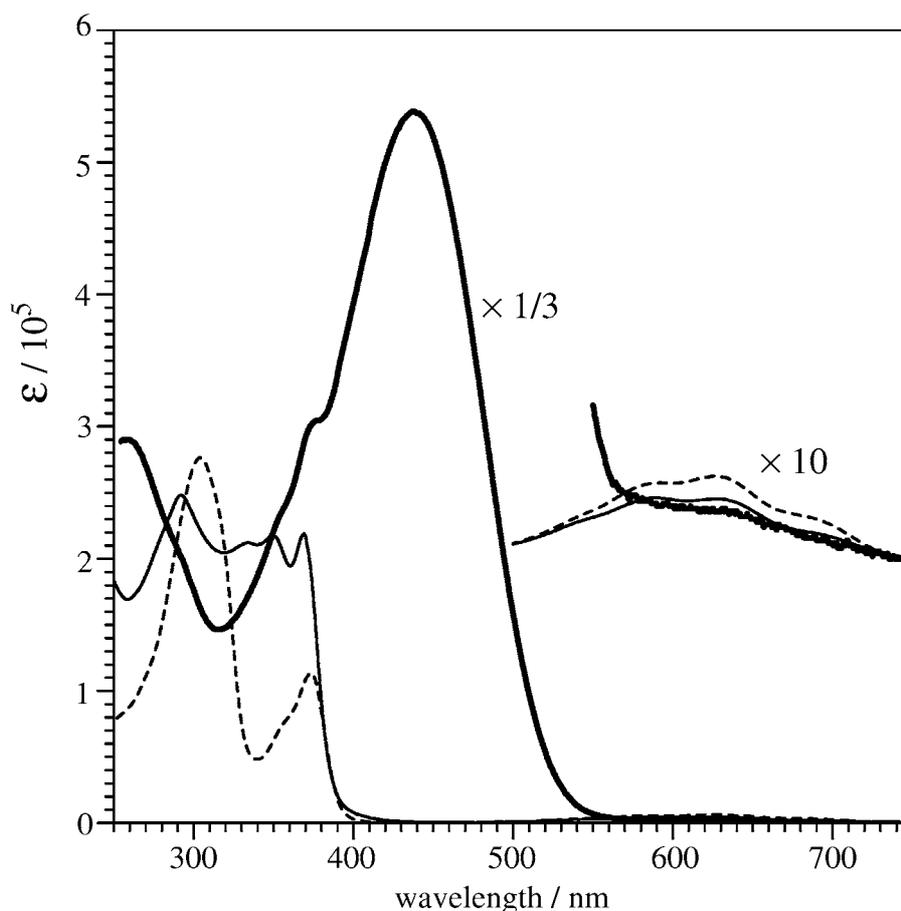
Figure 5. UV–Vis absorption spectra of thiophene–pyrrole hybrid oligomer type donor–radicals: Oligomer **6** (bold line), trimer **5** (thin line), and monomer **4** (dashed line).

2.2.3 Introduction of terminal sites

In order to utilize a spin–polarized molecule as a molecular spin device, it must be connected to electrodes through a terminal. Although a thiol group, which is chemisorbed to a gold substrate or a nanoparticle, is commonly utilized as a terminal unit, a nitronyl nitroxide radical reacts with thiols readily. We found that bis(*p*–NN–phenyl) disulfide constructs a dense self–assembled monolayer of π–radical thiols on a gold surface or gold nanoparticles through a reductive cleavage of the S–S bond [21,22]. As seen in these cases, in situ generation of a thiolate group is requested to keep the radical site intact.

An acetylthio group is easily converted to a thiolate group under a basic condition, such as aqueous ammonia [16,23]. It is, however, removed during the preparation of a nitronyl nitroxide radical. Therefore, ethoxycarbonylethylthio–derivatized oligomer **27** was prepared, following the reaction scheme shown in Figure 6. Accordingly, the ethoxycarbonylethylthio group was introduced to terthiophene derivative **22**. The advantage of dialkyl substituted terthiophene **22** is that it is free from the regioselectivity problem and also enhances the solubility of the final product. Then, its bromide **24** was coupled with distannylated trimer **14** to afford protected nonamer **25**, which was converted to nitronyl nitroxide **27** by the ordinal method. The ethoxycarbonylethylthio groups of

oligomer **27** can be removed in the presence of stronger base, such as sodium methoxide or diazabicycloundecene (DBU). Thus, introduction of the terminal sites to the spin–polarized molecular wire was successfully achieved.
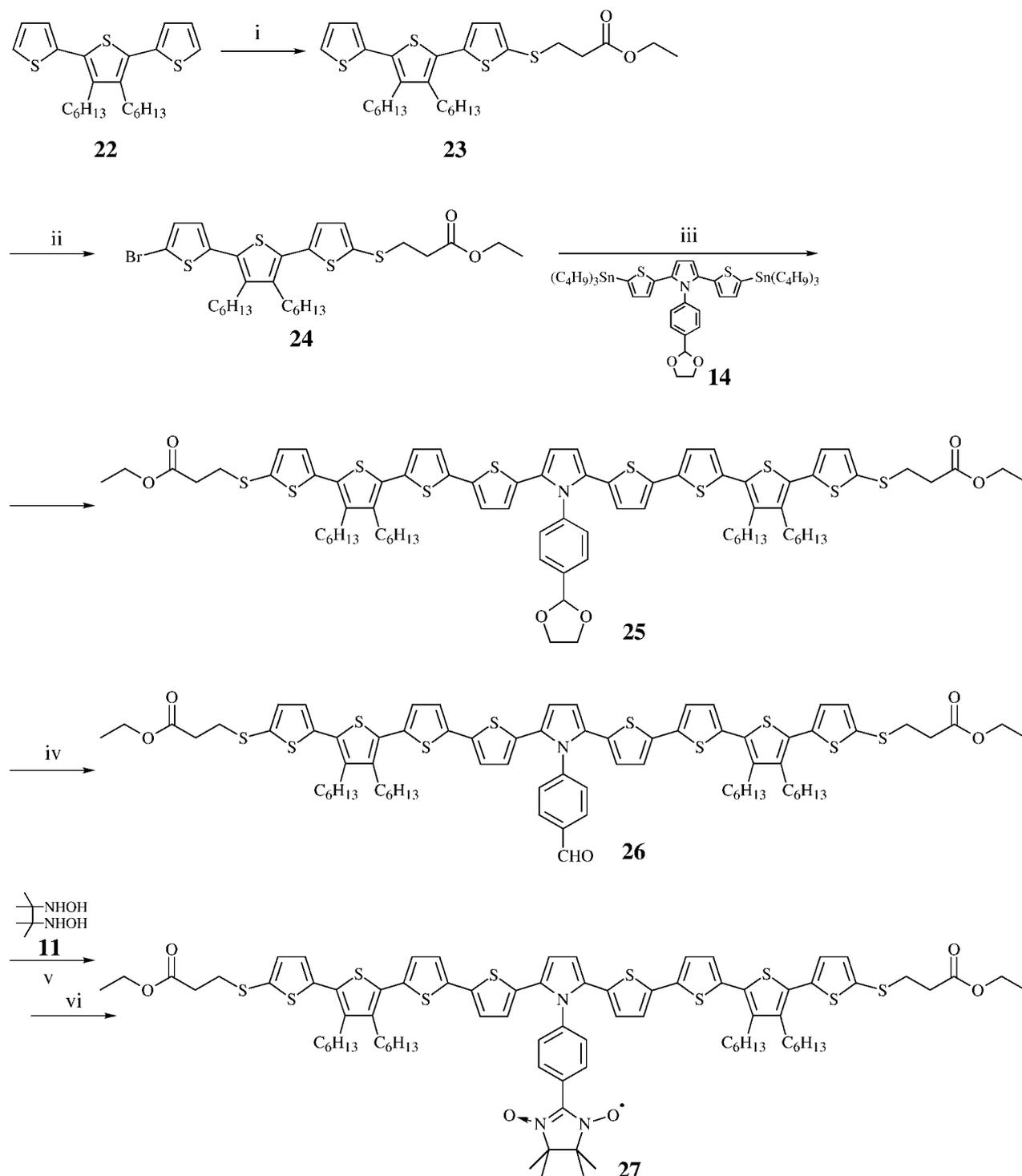
Figure 6. Synthetic scheme of the preparation of spin–polarized wire with terminal sites. Reagents and conditions: (i) 1) LDA, THF, −80°C to −50°C, 1 h, 2) S, THF, −50°C to −20°C, 2 h, 3) Br(CH$_2$)$_2$CO$_2$Et, THF, −20°C to r.t., 3 h, 40 %; (ii) NBS, DMF, r.t., 12 h, 65 %; (iii) **14**, Pd(PPh$_3$)$_4$, PhCH$_3$, 90°C, 36 h, 40 %; (iv) TsOH•H$_2$O, CHCl$_3$–acetone, r.t., 8 h; (v) **11**, **11**•H$_2$SO$_4$, PhH–MeOH, reflux, 8 h; (vi) PbO$_2$, K$_2$CO$_3$, PhH, r.t., 30 min.

2.3 Spin–Spin Interaction through Molecular Wire

For the present purpose, it is important to know how long the spin–polarization can be transmitted along the oligothiophene chain. Such a question may be answered by examining the magnetic property of oligothiophene–based biradicals, such as **28–30**.

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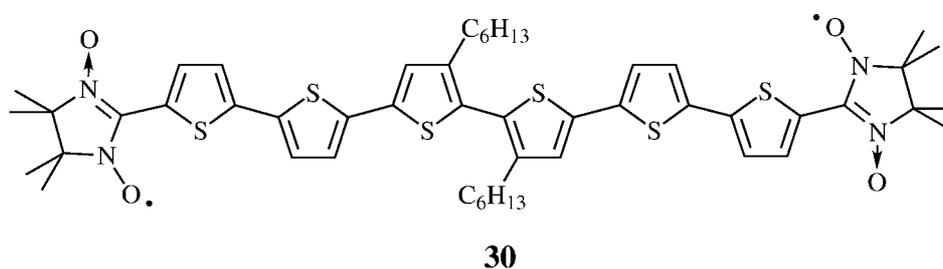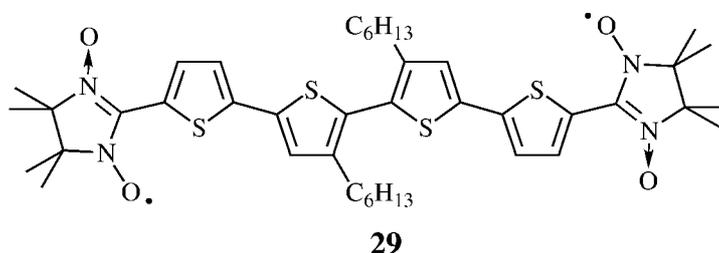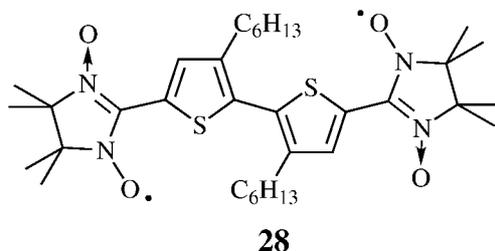
2.3.1 Preparation of oligothiophene–based biradicals

These oligothiophene–based biradicals were prepared as shown in Figure 7. Bromination of 3–hexylthiophene (**15**) by *N*–bromosuccinimide in chloroform – acetic acid at 0 °C afforded 2–bromo–3–hexylthiophene (**31**) selectively. A half amount of bromide **31** was converted to a Grignard derivative and was mixed with the other half. The reaction was catalyzed by Ni(dppp)Cl$_2$ to afford 3,3'–dihexyl–2,2'–bithiophene (**32**). Dilithiation of bithiophene **32** was performed in a refluxing diethyl ether. The dilithiated intermediate was reacted with dimethylformamide to afford dialdehyde **33**, while the addition of tri–*n*–butyltin chloride to the dilithiated intermediate afforded distannylated derivative **35**, which was coupled with the corresponding bromide **36** and **38** to afford dialdehydes **37** and **39**. These dialdehydes **33**, **37**, and **39** were converted to nitronyl nitroxides **28**–**30** according to the ordinary method. TOF MS **28:** m/z = 648 [M+3]$^+$, **29:** m/z = 811 [M+2]$^+$, **30:** m/z = 975 [M+2]$^+$.
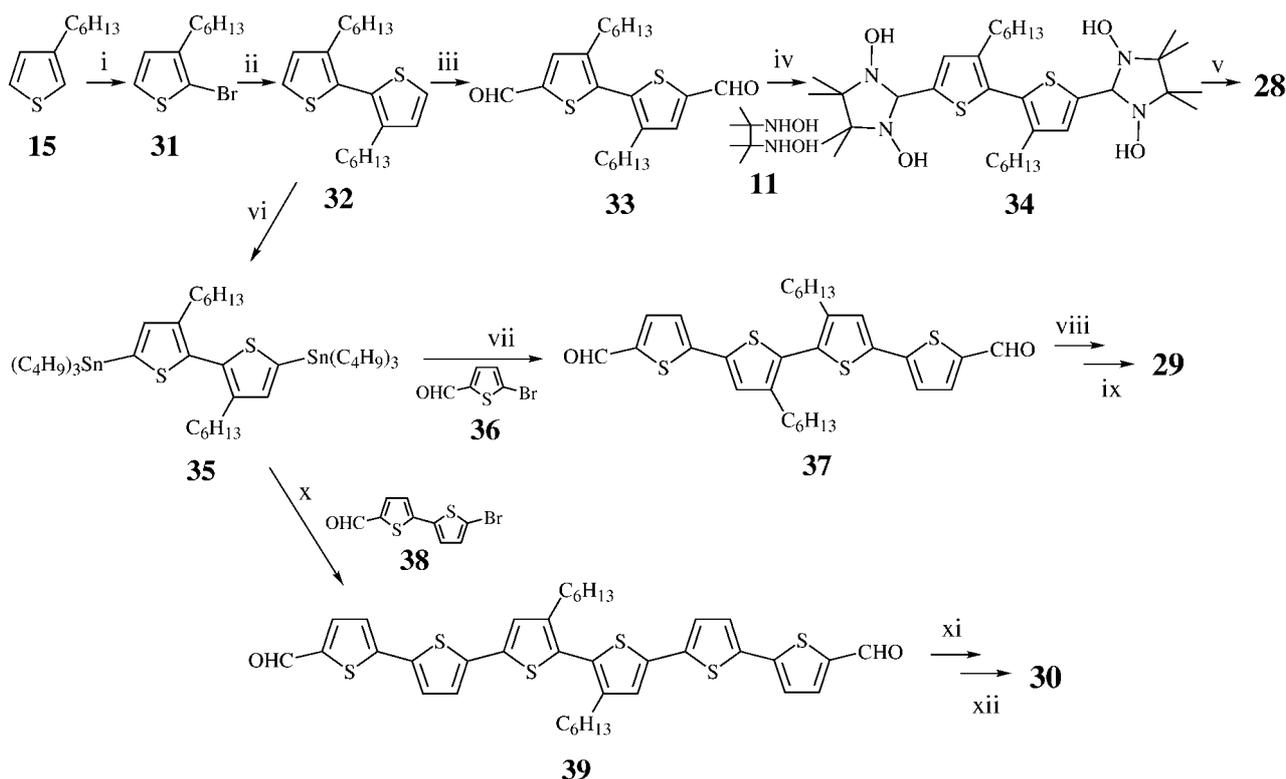
Figure 7. Synthetic scheme of the preparation of oligothiophene–based biradicals. Reagents and conditions: (i) NBS, CHCl$_3$–AcOH, 0°C, 2 h, 95 %; (ii) 1) Mg, Et$_2$O, reflux, 1 h, 2) Ni(dppp)Cl$_2$, Et$_2$O, reflux, 12 h, 85 %; (iii) 1) n–BuLi, Et$_2$O, –40°C to reflux, 4 h, 2) DMF, Et$_2$O, reflux, 2 h, 75 %; (iv) **11**, **11•**H$_2$SO$_4$, MeOH, reflux, 12 h, 35 %; (v) PbO$_2$, K$_2$CO$_3$, PhH, r.t., 12 h, 35 %; (vi) 1) n–BuLi, Et$_2$O, –30°C to reflux, 4 h, 2) n–Bu$_3$SnCl, Et$_2$O, reflux, 2 h, 95 %; (vii) **36**, Pd(PPh$_3$)$_4$, DMF, 70°C, 3 h, 75 %; (viii) **11**, **11•**H$_2$SO$_4$, PhH–MeOH, reflux, 12 h, 60 %; (ix) PbO$_2$, K$_2$CO$_3$, PhH, r.t., 10 h, 85 %; (x) **38**, Pd(PPh$_3$)$_4$, DMF, 70°C, 7 h, 50 %; (xi) **11**, **11•**H$_2$SO$_4$, PhH–MeOH, reflux, 12 h, 65 %; (xii) PbO$_2$, K$_2$CO$_3$, PhH, r.t., 12 h, 25 %.

2.3.2 Magnetic interaction between radical sites through neutral oligothiophene

Since ESR spectra of biradicals **28**–**30** show nine lines due to four equivalent nitrogen atoms (a_N = 0.38 mT), the electronic exchange between two radical sites is faster than the ESR time scale even when a sexithiophene is inserted. On the other hand, the magnetic interaction between two radical sites proved to be small on the basis of SQUID measurements of polycrystalline samples of the biradicals **28**–**30**. The details of the magnetic measurements of the biradicals **28**–**30** in the solid state will be published elsewhere.

2.3.3 Magnetic interaction between radical sites through oxidized oligothiophene

The cyclic voltammograms of these biradicals **28**, **29**, and **30** showed reversible first oxidation waves at +0.90 V, +0.87 V, and +0.84 V (*vs*. Ag/AgCl, in 0.1M n–Bu$_4$NClO$_4$/PhCN), respectively. Although the first oxidation potentials of these biradicals might be too high to be oxidized with iodine, cation triradicals of these derivatives were successfully generated. ESR spectra of the oxidized species of the biradicals showed a set of fine–structured signals (Figure 8). If these signals are attributed to quartet species [7], zero–field splitting parameters are $D = 0.0124$ cm^{-1} and $E =$

0.0009 cm^{-1} for **28**, D = 0.0125 cm^{-1} and E = 0.0009 cm^{-1} for **29**, D = 0.0125 cm^{-1} and E = 0.0008 cm^{-1} for **30**. These values of parameters are consistent with the electronic structure of cation triradicals of the oligothiophene–based biradicals. The result indicates that the generated π–spin is coupled ferromagnetically with both radical sites in the oxidized state.
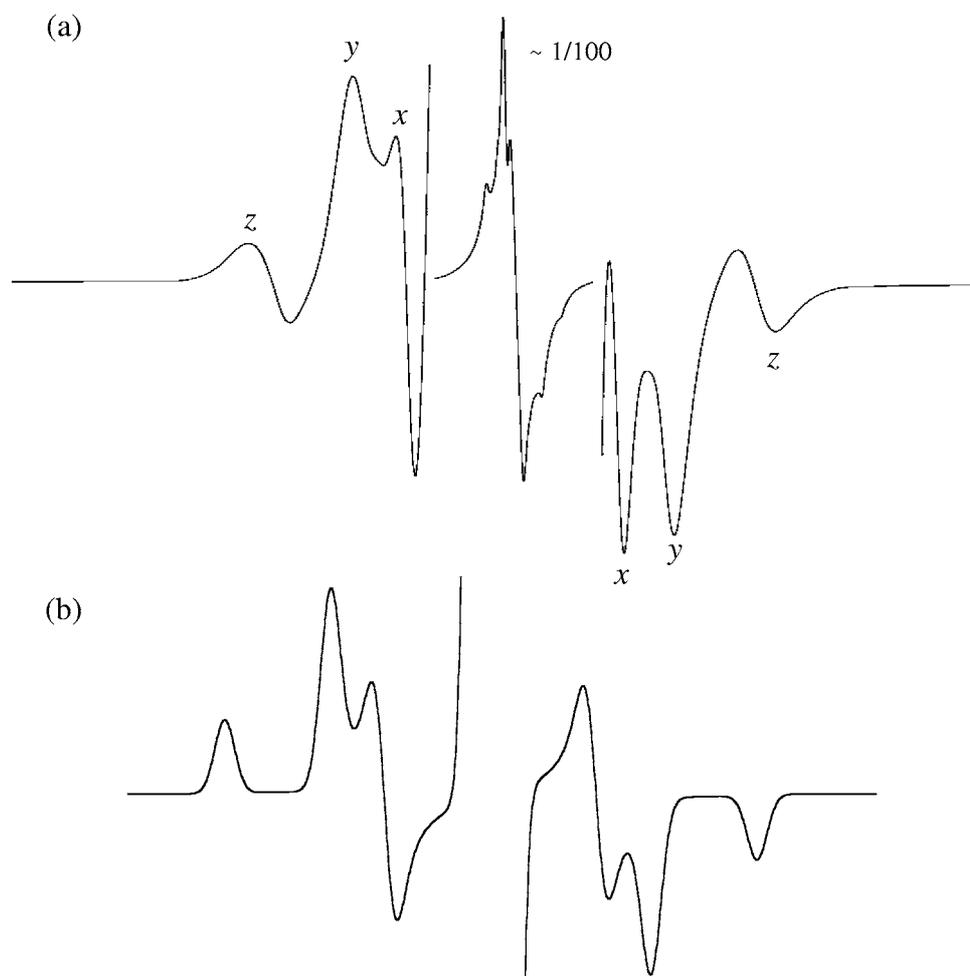

Figure 8. ESR spectra of the oxidized species of oligothiophene–based biradical **29**.
(a) Observed spectrum, (b) Simulated spectrum.

2.3.4 Electronic structure of oligothiophene–based biradicals

The examined oligothiophene–based biradicals **28–30** afforded quartet cation triradicals unexceptionally. The result indicates that the generated π–spin spreads over the entire molecule although the distance between two radical sites are as remote as 2.7 nm in the case of sexithiophene–based biradical **30**. In order to ensure this approximation, molecular orbital calculations based on the semiempirical PM3/UHF method were performed on the biradical **30**, in which two hexyl groups on the sexithiophene unit are replaced with hydrogen atoms. As deduced

from the experimental results, HOMO of the biradical **30** spreads over the entire molecule as shown in Figure 9, and its energy level is higher than those of two SOMOs on the each radical site. The coefficitents of two degenerated SOMOs (SOMO1 and SOMO2) are localized at the NN groups. Since SOMOs share coefficients at the NN groups with those of SOMO', which is derived from HOMO upon one–electron oxidation, the spins in relevant orbitals, SOMOs and SOMO', should be coupled ferromagnetically as shown in Figure 10.
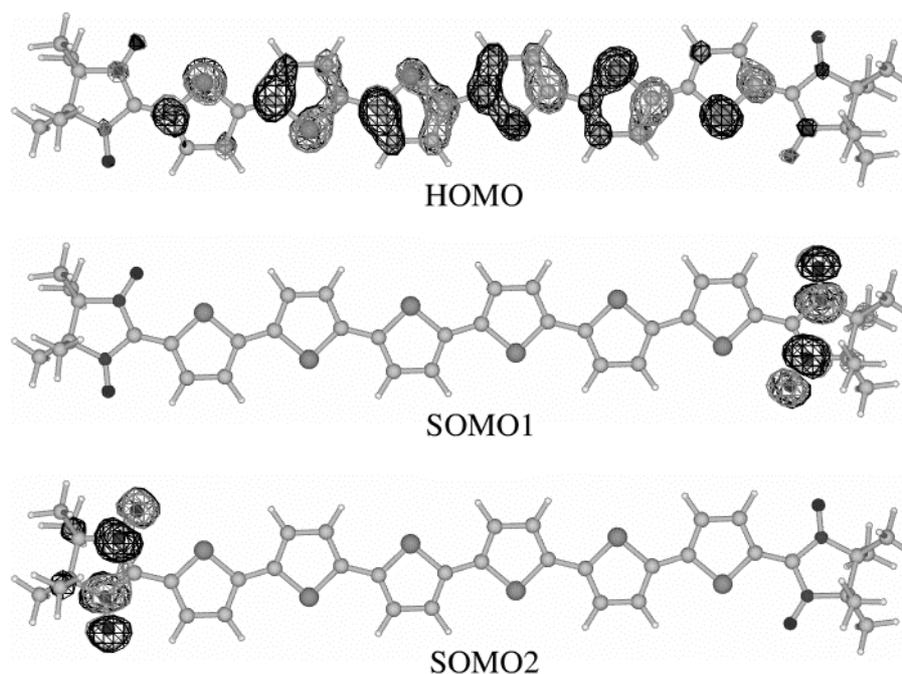
Figure 9. Molecular orbitals of oligothiophene–based biradical **30**.
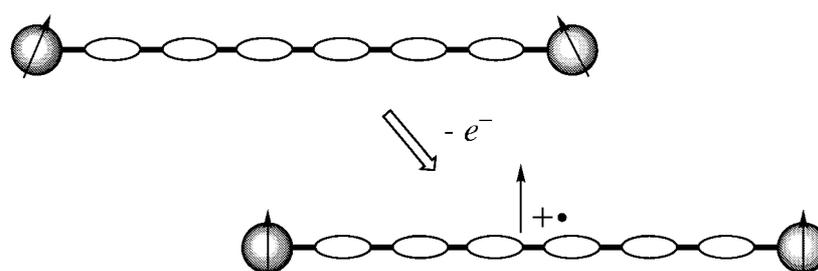
Figure 10. Schematic drawing of magnetic interactions in oligothiophene–based biradical **30**.

Although two nitronyl nitroxide radicals at both ends of an oligothiophene wire behave independently in a neutral state, they are coupled ferromagnetically only when the wire is singly oxidized. The result means that the spin–polarization caused by the radical site and that it can be transmitted along the wire as far as the number of monomers does not exceed six.

3 CONCLUSION

A spin–polarized molecular wire, which consists of a spin–polarized donor core, molecular wires, and terminal sites, was prepared as a prototypal unimolecular quantum spin device. We found that the pyrrole–based spin–polarized donor carrying oligothiophenes at both α–positions gave rise to a ground state triplet when it was singly oxidized. The potentiality of the molecular wire for transmitting the spin–polarized current has been proved in the case of an oligothiophene wire with two NN groups at both terminals. As far as the number of the monomer units does not exceed six, terminal NN groups couples ferromagnetically when the wire is singly oxidized.

When an oxidative voltage (a source–drain voltage) is applied to the spin–polarized molecular wire of which terminals are connected with electrodes, only an electron with a β–spin in HOMO is removed at the voltage corresponding to its first oxidation potential, provided that the spin of the unpaired electron of the radical site is α. This process is exactly the same as the cyclic voltammetric oxidation. The difference between the oxidation through terminals and in solution is that a β–spin electron is supplied instantaneously from the electrode in the former case once the wire is oxidized. As a result, a current of a β–spin passes through the molecular wire at the potential corresponding to the first oxidation potential of the molecular wire. The direction of the electronic spin should be maintained until the electron reaches the electrode, as discussed in the literature [24].
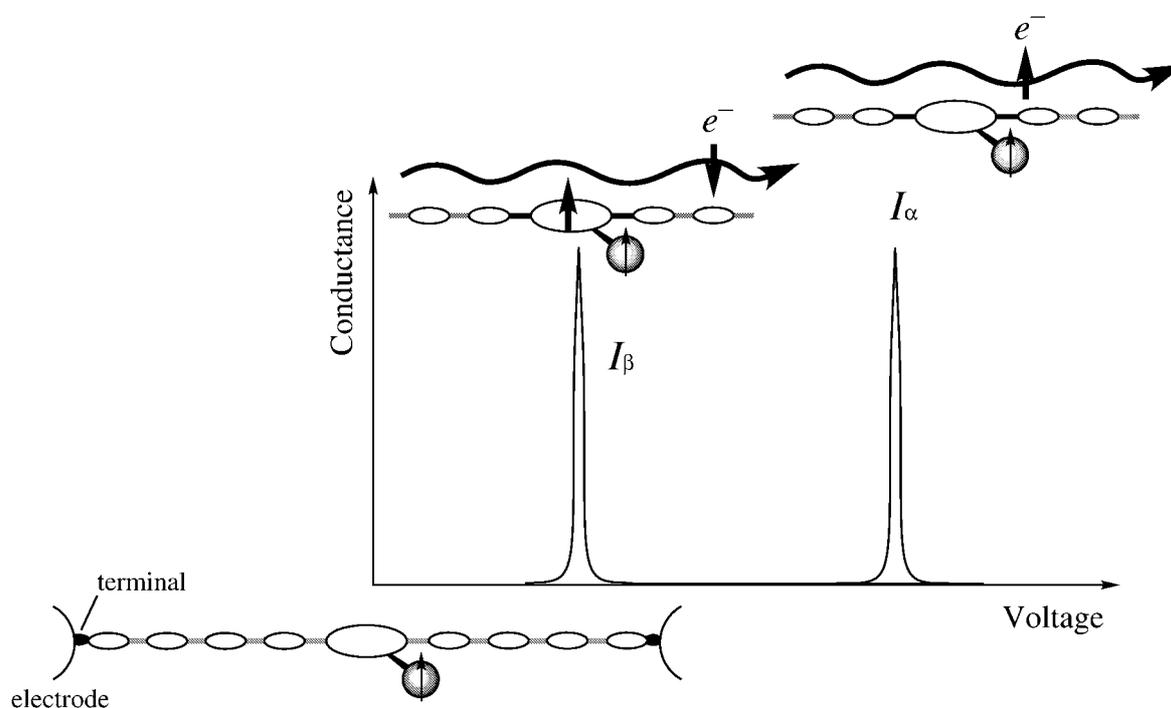
Figure 11. Plausible *I–V* characteristics of spin–polarized molecular wire.

When the oxidation voltage is further raised, an electron with an α spin in HOMO is removed and the wire passes the current of an α spin. Consequently, the spin–polarized molecular wire

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operates as a spin–rectifying device, passing the β–spin or the α–spin depending the range of the source–drain voltages.

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