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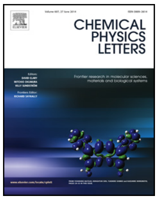

Spin conduction in nitroxide molecules

Yukihito Matsuura

Department of Chemical Engineering, Nara National College of Technology, Yatacho 22, Yamato-Koriyma, Nara 639-1080, Japan

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ABSTRACT

Spin conduction by a molecule-containing nitroxide radicals linked via a phenylene coupling unit was estimated by calculating the transmission of electrons in the molecule when sandwiched between two semi-infinite periodic gold crystals. Nitroxides linked via a *m*-phenylene coupling unit showed a large splitting in the energy of the transmission peaks of α- and β-spins, whereas this energy splitting was smaller for molecules with extended π-conjugation, such as nitroxides linked via a *p*-phenylene coupling unit. The energy splitting of transmission is influenced by spin polarization and constructive/destructive interference of radicals through the phenylene coupling unit.

1. Introduction

Organic molecules can be used for building the basic electronic components in molecular electronics [1–3], by applying a self-organization process [4], which can be described as a bottom-up approach. Analysis of the quantized conductance of a molecule sandwiched between metal electrodes provides a basic means of characterization of a molecular electronic device, either by experimental measurement or theoretical calculation [5–7]. Spintronics is another important application of molecular electronics [8]. Spintronic devices can be realized by the spin-filtering effect of a molecule or a crystal possessing unpaired electrons. Organic molecules are suitable for fabricating spintronic devices because of their weak spin-orbit interaction, which keeps the spin polarization within the limits of the molecule's length [9]. An organic molecule having several radicals linked through an *m*-phenylene coupling unit has been theoretically predicted to be a possible organic ferromagnetic material, since *m*-quinodimethane causes two degenerate molecular orbitals with a triplet ground state, according to Hund's rule [10]. Theoretical studies using the first-principles method suggest that cyclobutadiene, carbene, or other organometallic compounds in which the organic radicals combine with each other through the π-conjugated system will exhibit good spin-filtering efficiency [11–13].

A molecule-containing nitroxides is known to form stable radical species at ambient temperature [14]. The nitroxide radicals can be aligned in parallel through linkage to a *m*-phenylene group, and will exhibit a multiplet ground state. In particular, a molecule containing three nitroxide radicals linked through *m*-phenylene was synthesized and shown to exhibit a quartet state by ESR and magnetic measurements [15]. It is well known that molecules or crystals with unpaired electrons can exert a strong spin-filtering effect [11–13]. Owing to their air stability and low molecular weight, organic molecules with nitroxide groups are considered as promising materials for the preparation of nanomagnetic elements. In this study, several nitroxide-bearing molecules, in which the nitroxide radicals are linked through a *m*-phenylene group, are considered as spin carriers. Spin conduction in the nitroxide molecule sandwiched between gold electrodes will be examined by using the first-principles method.

2. Calculation method

The nitroxide radicals were linked to phenylene groups within the model molecules, with a bonding configuration in either the meta- or para-form. In addition, an oligomer of *m*-aniline, the reduced form of a molecule featuring meta-bound nitroxides, was chosen as a reference for the calculations. The ends of the molecule were bonded to the gold electrodes via phenylthiol groups, located in the para position of the terminal phenyl groups. The number of phenylene groups was expanded from two to four. The model molecules are defined as shown in Figure 1a.

The gold electrodes were modeled as three layers of Au(1 1 1) surface with a lateral (4 × 4) supercell, from which the semi-infinite left and right electrodes were constructed, as shown in Figure 1b. The Au–Au bond length was set to 2.88 Å. After optimization of the isolated model molecule, the hydrogen atoms were removed from the thiol groups to allow attachment at the interface of the semi-infinite left and right gold electrodes. The sulfur atom was located above the threefold hollow of the Au(1 1 1) surface, since this site was more energetically favorable than the other adsorption sites

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E-mail address: matsuura@chem.nara-k.ac.jp

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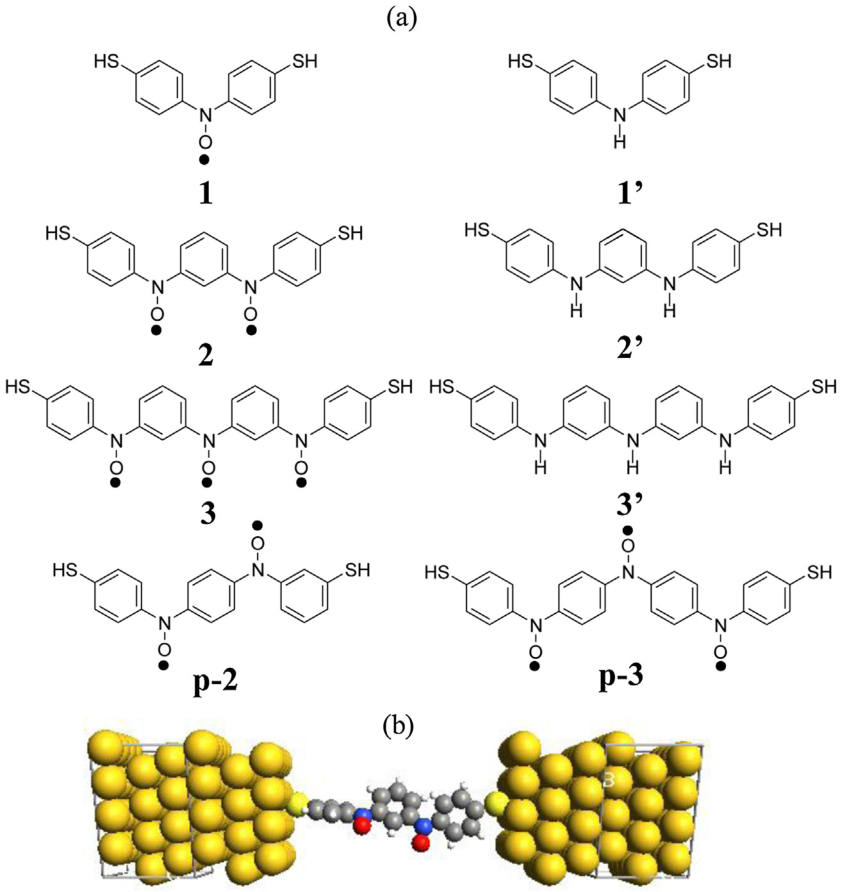

Figure 1. (a) Molecular structure of models for calculating the electrical conduction. (b) A molecule of 2 sandwiched between gold electrodes.

[16]. The S–Au distance (2.42 Å) was determined by varying the distance between the molecule and the gold surface until the total energy of the molecule attached to the gold supercell was minimized during the calculation of electrical conduction, as discussed below.

The electrical conductance calculated using the fully self-consistent NEGF-DFT method implemented in the Atomistix ToolKit software of QuantumWise A/S [17]. The calculations used approximate double-ζ basis sets with polarization functions and Troullier–Martins pseudopotentials [18]. The exchange-correlation potential for DFT can be calculated approximately using a generalized gradient approximation (GGA) within the Perdew–Burke–Ernzerhof (PBE) method [19,20].

The spin-dependent current I_σ (where σ denotes either α- or β-spin) in the central region was calculated from the Landauer–Büttiker formula [21,22]. The transmittance T_σ (E, V) of the σ-spin at an energy level E under a bias voltage of V was calculated from the retarded (advanced) Green's function and the contact broadening function derived from the left (right) electrode's self-energy, as described in reference. The conductance G_σ of the σ-spin was given by a linear expansion around $E = 0$ and $V = 0$. A total conductance of G was calculated from the sum of $G\alpha$ and $G\beta$. The shape of the molecular projected self-consistent Hamiltonian (MPSH) was also calculated to examine the spin conduction mechanism.

3. Results and discussion

Structural optimization of the molecules was carried out using a GAMESS program under B3LYP/6-31G** [23]. The optimized structure of molecule 1 was compared with an experimental result of a molecule having nitroxide radicals in reference [24]. In the optimized structure, N—O and N—C bond lengths were calculated to be 1.287 Å and 1.424 Å, respectively, and the O—N—C bond angle was 118.0°; these values showed good agreement with the experimental results of 1.289 Å, 1.413 Å, and 116.7°, respectively. Since the models of nitroxide-bearing molecules containing triphenyl or tetraphenyl coupling units should be optimized, the B3LYP/6-31G** level was adopted for the GAMESS program. The optimized structure of molecule 1 certainly exhibited a doublet state. Conversely, molecules 2 and 3 can exhibit two types of electron configuration, displaying triplet/singlet and quartet/doublet states, respectively. From the total energy of the optimized structures, a triplet state of 2 and a quartet state of 3 were adopted for the calculations of electrical conduction.

I nitially, to check spin transport of a molecule containing a single nitroxide group, the transmission spectra of molecules 1 and 1′ were calculated, as shown in Figure 2. The transmission spectrum of molecule 1′ displayed symmetrically shaped α- and β-spins because it is a closed-shell molecule. Although not shown here, molecules 2′ and 3′ followed similar trends in their transmission spectra. Conversely, the transmission spectrum of molecule 1 displayed asymmetrically shaped α- and β-spins, since degeneration was caused by an unpaired electron in the nitroxide group. Two peaks, at −0.34 eV for α-spin and 0.54 eV for β-spin, showed the same MPSH shape that was polarized at the nitroxide and phenylene groups, as shown in Figures 2b and 3.

Subsequently, spin transport in molecule 2 was examined, as shown in Figure 4a. The transmission spectrum of this molecule displayed the two transmission peaks, at −0.34 eV for α-spin and 0.12 eV for β-spin, in which the MPSH states were localized at