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Redox-switching of intramolecular magnetic interaction through π-conjugation mode change of 1,2-bis(4-dianisylamino)-1,2-bis(3-*N*-oxylamino)-substituted tetraarylethylene

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To develop the redox-switching system of intramolecular magnetic interaction, 1,2-bis[3-(*N*-*tert*-butyl-*N*-oxylamino)phenyl]-1,2-bis[4-{*N*,*N*-bis(4-methoxyphenyl)amino}phenyl]ethylene, tetraarylethylene with two nitroxide radical groups at the *meta*-position, was synthesized, and characterized by the electrochemical method and ESR spectroscopy. Cyclic voltammetry showed the tetraarylethylene core has the lower oxidation potential than the substituted nitroxide radical moiety. ESR spectroscopy in frozen solution revealed that the neutral form shows the fine-structured spectrum characteristic of the spin triplet species, while the dicationic form shows the anisotropic hyperfine-structured spectrum characteristic of the randomly-oriented nitroxide radical, indicating the drastic change of intramolecular magnetic interaction.

1. Introduction

An understanding of structure–property relationship in conjugated molecular materials provides a fundamental basis for molecular design of core units in molecule-based electronic devices. When the molecular structures are controllable by the external stimuli, the electronic properties inherent in the molecules can be efficiently switched on and off, which leads to the application to molecular switching and memory devices. In this context, it is well known that tetraarylethylenes exhibit the drastic change in their molecular structures through the redox reaction; that is to say, the $C=C$ double bond is elongated like a $C-C$ single bond and concomitantly rotational motion about the olefinic bond takes place. Such a free rotation was experimentally confirmed by reversal coulometric experiments. For example, when the *cis*-form of 1,2-bis(4-dimethylaminophenyl)-1,2-diphenylethylene was subjected to two-electron-oxidation and subsequent two-electron-reduction, the NMR spectrum of the reduced neutral product gave the evidence for the mixture of *cis*- and *trans*-isomers [1]. More unequivocal evidence was afforded by the X-ray structural analyses of the isolated mono- and dications of 1,1,2,2-tetrakis(4-methoxyphenyl)ethylene, in which the rotational angle around ethylenic $C-C$ bond increases on going from the neutral through the monocationic to the dicationic states [2].

Such a drastic structural change including π-conjugation mode change can be utilized as a redox-switchable spin coupling unit. For instance, the interconversion of intramolecular magnetic interactions between two radical moieties has been achieved by using 1,2-bis(3-thienyl)ethene and 1,2-bis(2-thienyl)ethene as a photoswitchable spin coupling unit [3]. To create a new type of redox-switchable intramolecular magnetic interaction converting organic molecules, it has been designed and synthesized, the novel tetraarylethylene carrying two nitroxide radical groups, 1,2-bis[4-(*N*-*tert*-butyl-*N*-oxylamino)phenyl]-1,2-bis[4-{*N*,*N*-bis(4-methoxyphenyl)amino}phenyl]ethylene (**1**) [4]. The neutral **1** showed a strong antiferromagnetic interaction through π-conjugated network between radical centers. On the other hand, the spin–spin correlation in $\mathbf{1}^{2+}$ disappeared in conjunction with interception of π-conjugation between two nitroxide radical groups (Scheme 1). In this work, 1,2-bis[3-(*N*-*tert*-butyl-*N*-oxylamino)phenyl]-1,2-bis[4-{*N*,*N*-bis(4-methoxyphenyl)amino}phenyl]ethylene (**2**) as the structural isomer of **1** was investigated by means of electrochemistry and ESR spectroscopy.

2. Results and discussion

2.1. Synthesis

The synthesis of bisnitroxide **2** was carried out by the similar route with that of **1**, which is outlined in Scheme 2. Monolithiated 1,3-dibromobenzene was coupled with 2-methyl-2-nitrosopropane to give hydroxylamine **3**. The hydroxylamine **3** was protected

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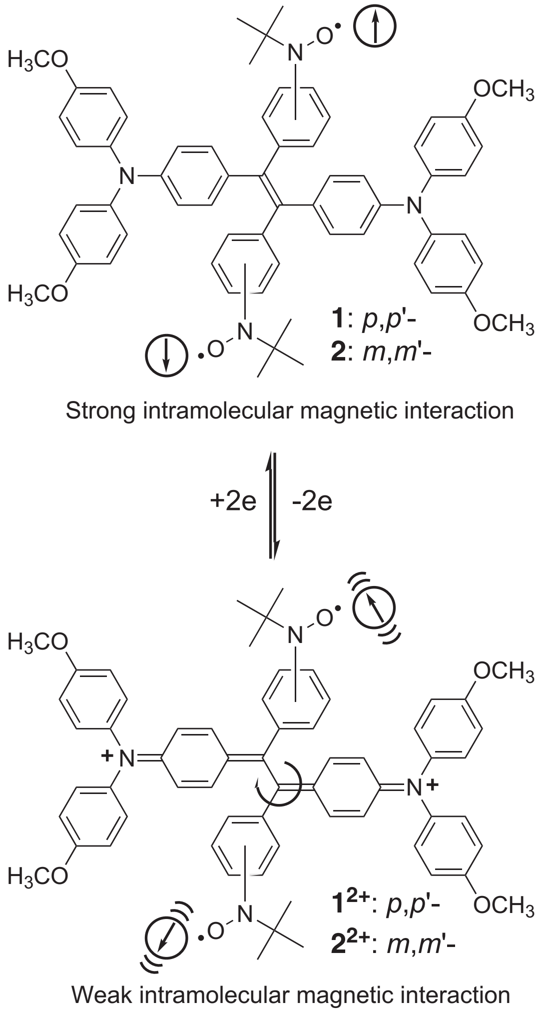
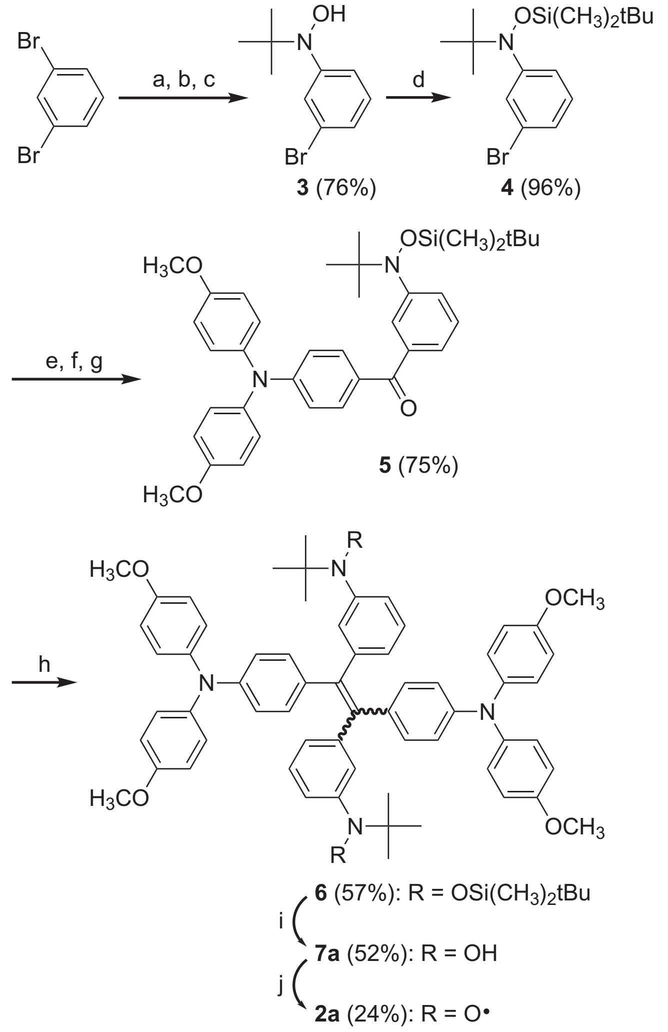


Scheme 1. Redox-switching of through-bond magnetic interaction.



Scheme 2. Synthetic route for diradical **2**. Reagents: (a) *n*-BuLi, THF; (b) *t*-BuNO, THF; (c) aqueous NH_4Cl; (d) *t*-$Bu(CH_3)_2SiCl$, imidazole, DMF; (e) *n*-BuLi, THF; (f) 4-{bis(4-methoxyphenyl)amino}benzonitrile, THF; (g) H_2O; (h) $TiCl_4$, Zn, pyridine, THF; (i) *n*-Bu_4NF, THF; and (j) Ag_2O, CH_2Cl_2.

with *tert*-butyldimethylsilyl group to afford **4** [5]. Asymmetrically substituted diarylketone **5** was prepared by addition of 4-{bis(4-methoxyphenyl)amino}benzonitrile to the lithiated **4** and the subsequent hydrolysis. The reductive coupling of the ketone **5** with a low-valent titanium reagent [6] gave **6a** (*trans*-isomer) and **6b** (*cis*-isomer) at the ratio of **6a**/**6b** = 78/22. Here, we regarded **6a** as the *trans*-isomer because the ESR spectrum for **2a** derived from **6a** indicates that **2a** takes the *trans* configuration (see Section 2.3). After desilylation of **6a** with tetrabutylammonium fluoride, the desired bisnitroxide **2a** was obtained by oxidation of **7a** with Ag_2O. Bisnitroxide **2a** was unstable as compared with *para*-nitroxyl-substituted **1**. The instability of this kind of nitroxide seems to be ascribed to the isomerization to aminoquinone imine *N*-oxide [7]. However, the ESR spectrum of bisnitroxide **2a** in toluene under an argon atmosphere after 4 days was nearly-unchanged. In this study, the freshly-prepared sample was used for all measurements in order to avoid the impurity incorporation.

2.2. Electrochemistry

The effective conversion of intramolecular magnetic interaction before and after the oxidation of **2a** postulates the lower oxidation potential of tetraarylethylene core than the two nitroxide groups. The cyclic voltammogram of **2a** measured in 1 mM benzonitrile solution is shown in Fig. 1. In comparison with the first oxidation potentials of the non-nitroxyl-substituted tetraarylethylene (**8**) [8] and the *N*-*tert*-butyl-*N*-phenylnitroxide (**9**) [9] (Scheme 3), it is concluded that the first quasi-two-electron transfer process corresponds to the oxidation of the tetraarylethylene core, while the second irreversible two-electron transfer process to the oxidation of the two nitroxide radical groups (Table 1). This is also supported by the electronic structure of model compound calculated at the UB3LYP/6-31G(d,p) level of theory (Table S1 and Fig. S2). The orbital energy of singly occupied molecular orbitals (SOMOs) localized on the nitroxide groups is lower than that of HOMO distributed over the tetraarylethylene core. The same situations are reported in the literature [10]. The observed separation of the anodic and cathodic peak potentials for the first redox process (68 mV) is larger than the theoretical value of 28 mV for the reversible two-electron transfer process [11]. This indicates that the first oxidation wave of **2a** is the overlap of two closely-spaced consecutive one-electron-oxidation processes. The similar redox behavior is also observed for 1,1,2,2-tetrakis(4-methoxyphenyl)ethylene in a polar solvent like acetonitrile [1]. In **2a**, the redox process of the tetraarylethylene core approaches a two-electron transfer, whereas two resolved one-electron-transfer redox waves were observed in *para*-nitroxyl-substituted **1** [4] (Fig. S5). This contrast is closely related to the fact that the *para*-substituting nitroxide radical groups affect the oxidation process of the tetraarylethylene core through