

Tetraarylethylene having two nitroxide groups: redox-switching of through-bond magnetic interaction by conformation change†

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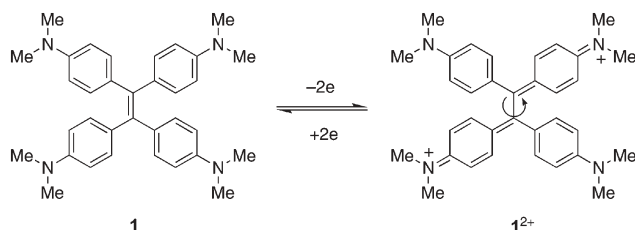
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Reversible redox-switching of through-bond magnetic interaction has been achieved by conformation change of the tetraarylethylene moiety upon redox input: intramolecular magnetic interaction between two nitroxide groups is dead after oxidation, whereas it was alive before.

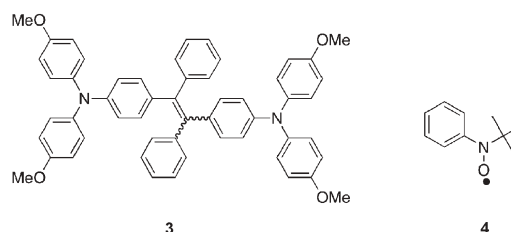
Sterically congested hydrocarbon molecules often exhibit remarkable structural changes upon redox input.¹ Upon oxidation of tetraphenylethylene (TPE), the C=C double bond is elongated to a C–C single bond and concomitantly rotational motion about the olefinic bond takes place. X-Ray structural analyses of the isolated mono- and di-cations of TPE derivatives revealed that the rotational angle increases on going from cation to dication.² In conjunction with this intriguing structural change, TPE has attracted much attention from the viewpoint of new electrochromic systems.³ In particular, tetrakis(4-dimethylaminophenyl)ethylene (**1**) can be reversibly converted to the diamagnetic dication (**1**²⁺) in which the two cyanine moieties⁴ are generated by rotational motion about the olefinic bond.³ Hence, **1** is recognized as a novel organic electrochromic system with long wavelength absorptions and high extinction coefficients.



On the other hand, the drastic structural change in TPE including the change of π -conjugation connection pathway can be utilized as a redox-switchable magnetic coupling unit. To date, although a large number of studies have been made on the redox-generation of non-Kekulé high-spin organic molecules,⁵ little is known about the control of through-bond magnetic interactions using interconversion of the π -conjugation pathway.⁶ To create a new type of organic electrochromic system having a function of a redox-switch of through-bond magnetic interactions, we have designed the novel TPE derivative carrying two nitroxide radicals (**2**), which was synthesised as a mixture of *cis*- and *trans*-isomers (ESI†). In the neutral form of **2**, a

strong exchange interaction (J) through the π -conjugated network^{7a} is expected between the two radical centers. On the other hand, the through-bond magnetic interaction in the dication **2** disappears the interception of π -conjugation between the two nitroxide groups originating from rotational motion about the olefinic bond (Scheme 1). In other words, the TPE moiety of **2**²⁺ is considered to have a twisted tetramethylenethane (TME) structure, in which singlet and triplet states are virtually degenerate ($J \approx 0$).⁷

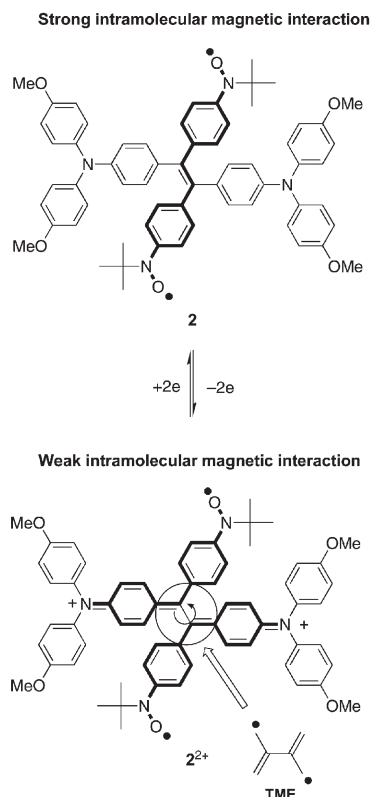
Effective conversion of through-bond magnetic interaction after and before oxidation of **2** postulates a lower oxidation potential of the TPE moiety than the two nitroxide groups. The cyclic voltammetry of **2** in 1 mM benzonitrile solution was carried out (Table 1). In comparison with the first oxidation potential of the non-nitroxide-substituted TPE (**3**: *cis*-*trans* mixture)⁸ and the *N*-*tert*-butyl-*N*-phenylnitroxide (**4**),⁹



it was confirmed that the first two consecutive reversible one-electron transfer steps correspond to the oxidation of the TPE moiety, while the third step two-electron transfer process to the oxidation of the two nitroxide groups. The observed peak separations of 74, 70, and 69 mV for the first to third redox processes were larger than the theoretical value of 56.5 mV (25 °C).¹⁰ All these peak separations are probably caused by the *cis*-*trans* mixture of the present sample.

The EPR spectrum of **2** in a frozen toluene matrix (123 K) showed a fine-structured spectrum characteristic for the spin triplet species [Fig. 1(a)]. The forbidden $\Delta M_S = \pm 2$ resonance was also detected in a half-field region of the allowed $\Delta M_S = \pm 1$ resonance, indicating the existence of spin triplet species.¹¹ Moreover, it was clarified that the two nitroxide groups of **2** are antiferromagnetically coupled from the temperature dependence of the molar magnetic susceptibility (χ_M) of the powder sample measured by the SQUID magnetometer (Fig. 2). The $\chi_M T$ value decreases with decreasing temperature from 0.75 emu K mol⁻¹ corresponding to two independent spins of 1/2 to 0 emu K mol⁻¹, corresponding to two antiferromagnetically coupled spins of 1/2. The measured data were analyzed on

† Electronic supplementary information (ESI) available: synthetic details for **2**. See <http://www.rsc.org/suppdata/cc/b4/b410858b/>
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Scheme 1 Bisnitroxide **2** (*trans*-isomer) and the redox-switching of through-bond magnetic interaction.

Table 1 Redox potentials (V) of **2** and its related compounds^a

Compound	E_1°	E_2°	E_3°
2	0	0.25	0.49 ^b
3	0.15 ^b		
4	0.41 ^c		

^a 0.1 M *n*-Bu₄NBF₄ in PhCN, potential vs. Fc/Fc⁺, Pt electrode, 25 °C, scan rate 100 mV s⁻¹. ^b Two-electron oxidation process. ^c Irreversible oxidation process represented by the anodic peak potential.

the basis of eqn. (1),

$$\chi_M T = f_1 \frac{2N_A g^2 \mu_B^2}{k_B} \frac{1}{3 + \exp\left(-\frac{2J_1}{k_B T}\right)} + f_2 \frac{2N_A g^2 \mu_B^2}{k_B} \frac{1}{3 + \exp\left(-\frac{2J_2}{k_B T}\right)} + (1 - f_1 - f_2) \frac{N_A g^2 \mu_B^2}{2k_B} \quad (1)$$

where f_1 and f_2 are the molar fractions of the two isomers, J_1 and J_2 the magnetic exchange coupling constants (the positive and negative values indicate ferromagnetic and antiferromagnetic interactions, respectively) for the two isomers, N_A the Avogadro number, g the isotropic g -factor, k_B the Boltzmann constant, and μ_B the Bohr magneton. The first two terms represent the Bleaney–Bowers singlet–triplet model¹² corresponding to the two isomers,

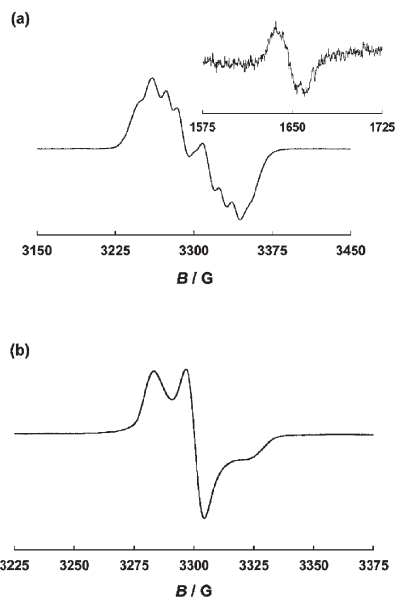


Fig. 1 EPR spectra of (a) **2** in toluene at 123 K (inset: the forbidden $\Delta M_S = \pm 2$ resonance at 123 K), and (b) **2** after treatment with 2 equiv. of TBA·SbCl₆ in toluene/*n*-butyronitrile (1 : 1) at 123 K.

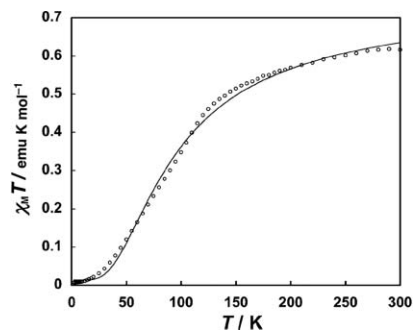


Fig. 2 Plot of $\chi_M T$ versus T for **2** at 500 G. The solid line represents the best theoretical fit [eqn. (1)] to the data.

and the third is the Curie term originating from a very small quantity of spin doublet impurity such as mononitroxide radicals. The best fitted values for f_1 , f_2 , J_1 , and J_2 were estimated to be $f_1 = 0.27$, $f_2 = 0.71$, $J_1/k_B = -66$ K (-0.13 kcal mol⁻¹), and $J_2/k_B = -93$ K (-0.18 kcal mol⁻¹), indicating intramolecular antiferromagnetic interaction for both isomers. Moreover, the ratio of the two isomers in **2** can be estimated at 28 : 72 from f_1 and f_2 values. From the DFT calculations at the UB3LYP/6-31G* level,¹³ the ground states for *cis*- and *trans*-isomers of **2** were predicted to be both singlet state, and the singlet *trans*-isomer lies 0.24 kcal mol⁻¹ lower than the singlet *cis*-isomer. This suggests that the *trans*-isomer is the thermodynamically favorable isomer. In addition, the energy differences between the singlet and triplet states $\Delta E_{S-T} (= 2J)$ for *cis*- and *trans*-isomers were predicted to be -0.47 and -0.49 kcal mol⁻¹, respectively. This indicates that the *trans*-isomer has a large J value as compared with the *cis*-isomer. Therefore, f_1 and f_2 are likely to be assignable to the *cis*- and *trans*-isomers, respectively.

On the other hand, when 2 equiv. of tris(4-bromophenyl)ammonium hexachloroantimonate (TBA·SbCl₆) are added to **2** in toluene/*n*-butyronitrile (1 : 1) solution at 195 K, the EPR spectrum of **2**²⁺ was completely changed from that observed for neutral **2** to one with typical anisotropic hyperfine structure for the randomly oriented mononitroxide radical [Fig. 1(b)]. This strongly indicates that the two nitroxide groups in **2**²⁺ are no longer coupled magnetically due to rotational motion about the olefinic bond. Note that the principal value (*A*_{ZZ})¹⁴ for the perpendicular direction to the nitroxide plane of the hyperfine coupling tensor of **2**²⁺ takes a small value (19.28 G) as compared with the corresponding value (27.99 G) of **11**. This suggests that spin density on the nitrogen atoms of the nitroxide groups decreases on going from **2** to **2**²⁺, reflecting the spin delocalization over the whole molecule.

To check the reversibility between **2** and **2**²⁺, **2**²⁺ was treated with an excess of hydrazine monohydrate. Consequently, the same EPR spectrum as the as-prepared **2** [Fig. 1(a)] was retrieved from the hyperfine-structured spectrum due to the independent nitroxide radical of **2**²⁺ [Fig. 1(b)]. From the viewpoint of redox-switching of through-bond magnetic interaction, on- and off-states correspond to the *cis*-*trans* mixture of **2** and the dication **2**²⁺, respectively. In addition, the reversibility was also confirmed spectroelectrochemically. Absorption spectra for **2**²⁺ at a forward bias of +0.4 V vs. Fc/Fc⁺ and **2** at a reverse bias of -0.1 V vs. Fc/Fc⁺ are shown in Fig. 3. Several electrochemical cycling experiments reversibly reproduced the spectra corresponding to **2** and **2**²⁺ (Fig. 3). These results strongly suggest that the present diradical **2** can operate as a redox-switch of through-bond magnetic interaction. It is anticipated that current investigations will lead to more versatile switching systems when the radical centers are incorporated into TPE so as to create the required through-bond magnetic interactions.

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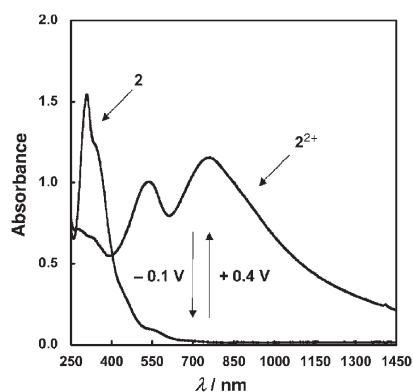


Fig. 3 Absorption spectral change of **2** in CH₂Cl₂ at room temperature upon several electrochemical cycling episodes between +0.4 and -0.1 V vs. Fc/Fc⁺.

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