Robust Triplet Molecule: Cationic Diradical of 3,4′-Bis(diphenylamino)stilbene

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Received May 14, 1999
Revised Manuscript Received June 14, 1999

The prospect of realizing a purely organic-based and unknown magnetic material has led to the continued synthetic research on π-conjugated but non-Kekulé-type and high-spin organic molecules.[1] For example, Rajca et al.[2] recently demonstrated a spin quantum number (S) of average ${}^{20}/_{2}$ at low temperature by precisely synthesizing dendric−macrocyclic poly(1,3-phenylenephenylmethine)s. However, there remained the following requirements to allow a very large S value: chemical stability of the radical group as a spin source, insensitivity to spin defects that break down π-conjugation, and a long-distance interaction to align even remote spins. These become more important with an increase in the molecular size of the organic radical molecule. One of the potential candidates to satisfy these requirements and to realize a very high-spin molecule is a π-conjugated polymer bearing multiple pendant radical groups, which are connected to the π-conjugated backbone to satisfy the non-Kekulé structure. The advantages of the pendant-type polyradicals with regard to the requirements have been partially substantiated by an experimental study on poly(4-oxyphenyl-1,2-phenylenevinylene):[3] (i) A stable radical species can be introduced to the backbone as the pendant group. (ii) The spin alignment is not sensitive to spin defects because a ferromagnetic exchange between spins occurs through the π-conjugated backbone. And (iii) the ferromagnetic interaction works over a long distance through the backbone among not only their neighboring spins but also remote spins. The poly(1,2-phenylenevinylene) backbone was characterized as being relatively coplanar with extended π-conjugation even after the introduction of pendant groups.

Chart 1

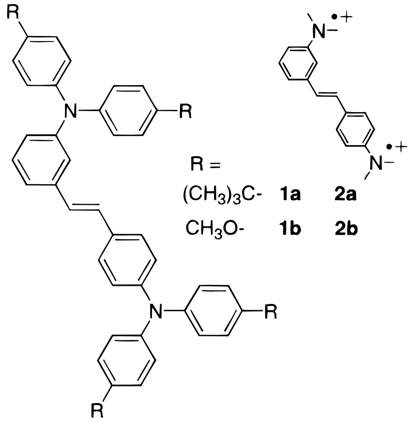
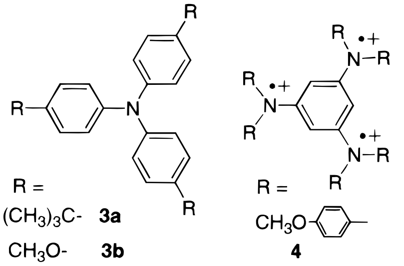


Chart 2



In this communication, we used along this promising strategy of the pendant polyradicals and have for the first time synthesized the pendant-type cationic diradical compound, 3,4′-bis(diphenylaminium)stilbene **2**, shown in Chart 1. It is known that triarylaminium radicals (examples, the cationic radicals of **3** in Chart 2) are significantly stable and that their spin density is delocalized into the aryl groups.[4] The di- and tri-(cationic radical)s of *m*-phenylene- or 1,3,5-benzenetriyl-linked triarylamines, e.g., **4**, have been theoretically and experimentally investigated to reveal their ground-state triplet and quartet and ferromagnetic coupling capability of the *m*-phenylene and 1,3,5-benzenetriyl unit.[5] Bushby et al. extended these di- and triradicals into a networked polyarylamine polymer; its cationic radical, cross-conjugatively formed in the backbone, displayed $S = {}^{8}/_{2}$.[6] However, no study has been reported on the pendant-type cationic multiradical compounds. The stilbene framework in **2** corresponds to the dimer unit of the poly(4-radical substituted-1,2-phenylenevinylene);[3] a high-spin alignment is predicted by simple enumeration of the spin-exchange communication schematically represented by the up−down small arrows in the stilbenoid unit of Chart 3 (big arrows = spin at the radical center). The ferromagnetic coupling effect of the 3,4′-stilbene linker has been computationally discussed and also experimentally studied using the bis(2′,6′-di-*tert*-butyl-4′-oxyphenyl) and bis(*N*-*tert*-butylnitroxide) derivatives.[7] In this paper, we describe the successful formation of a thermally stable and triplet cationic diradical by optimizing the radical generation from **2**.

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[2] (a) Rajca, A.; Wongsriratanakul, J.; Rajca, S. *J. Am. Chem. Soc.* **1997**, *119*, 11674. (b) Rajca, A.; Wongsriratanakul, J.; Rajca, S.; Cerny, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1229.

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[6] (a) Bushby, R. J.; Ng, K. M. *Chem. Commun.* **1996**, 659. (b) Bushby, R. J.; Gooding, D. *J. Chem. Soc., Perkin Trans. 2.* **1998**, 1069.

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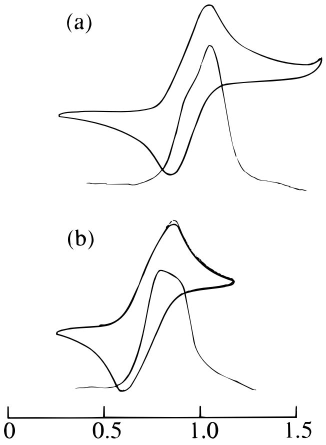
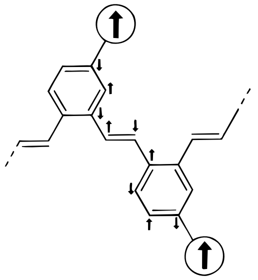


Figure 1. Cyclic voltammograms (scanning rate = 100 mV/s) and differential pulse voltammograms for **1a** (a) and **1b** (b) in CH_2Cl_2 with 0.1 M $(C_4H_9)_4NBF_4$ as a supporting electrolyte, at room temperature.

Chart 3



3,4′-Dibromostilbene was prepared by coupling 3-bromostyrene and 1-bromo-4-iodobenzene, and it was cross-coupled with *N*,*N*-di(*p*-*tert*-butyl- or *p*-methoxyphenyl)-amine using a catalyst of $Pd_2(dba)_3$ and P(*o*-tolyl)$_3$ to yield 3,4′-bis[*N*,*N*-di(*p*-*tert*-butylphenyl)amino]stilbene **1a** and 3,4′-bis[*N*,*N*-di(*p*-methoxyphenyl)amino]stilbene **1b**.

Cyclic voltammetry of **1** in CH_2Cl_2 showed complete reversible oxidation and reduction waves (Figure 1). Differential pulse voltammetry gave two oxidation responses ascribed to the two amine sites. The π-conjugation and/or steric distance in the stilbene linkage of **1** separate the first and second oxidation steps due to cation−cation repulsion. The overall redox potentials (vs Ag/AgCl) were 0.93 and 0.75 V for **1a** and **1b**, respectively, which were appropriately anodically shifted in comparison with the potentials of the corresponding triarylamines (0.89 and 0.65 V for **3a** and **3b**, respectively). The potentials were also explained by the electron-donating effect of the *tert*-butyl and methoxy groups. The cyclic voltammogram was reversibly recorded in the repeated potential sweeps at room temperature. This result means that the cationic radical is stable even at room temperature and that the radical generation is not accompanied by a subsequent side reaction such as dimerization to form a benzidine derivative.

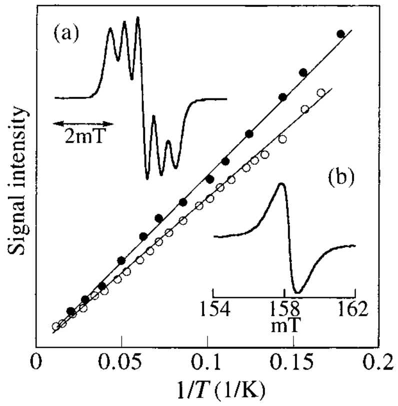


Figure 2. Curie plots for the peak in the $\Delta M_s = \pm 2$ region for the diradical **2a** (○) and **2b** (●) with spin concentration = 0.66 and 0.91 spin/N unit, respectively, in the POE/CH_2Cl_2 glass. Inset a: ESR spectrum of the radical of **1a** with spin concentration = 0.05 spin/N unit at $g = 2.0026$. Inset b: ESR $\Delta M_s = \pm 2$ spectrum for **2a**.

The oxidation peak potentials for **1a** and **1b** were 1.02 and 0.85 V, respectively (see Figure 1). $NOBF_4$ was selected as the oxidizing agent of **1** in response to these potentials. A CH_2Cl_2 solution of **1** turned deep blue (λ_{max} = 689 and 769 nm for **1a** and **1b**, respectively) by oxidation using a small excess of $NOBF_4$ solubilized in CH_2Cl_2 with poly(oxyethylene) (POE, mol wt = 2.0×10^4, [POE]/[**1**] = 100). The radical formation was supported by the appearance of the ESR signal; the spin concentration increased beyond 0.9 spin/N unit for **2b** which was estimated at room temperature under the assumption of $S = {}^1/_2$ from integration of the ESR signal intensity compared with the solution of 2,2,6,6-tetramethyl-1-piperidinyloxyl. The half-life of the radical estimated by ESR was 2.5 day for **2b** in the solution at room temperature, which was much longer than those reported for the *m*-phenylene-coupled oligo(triarylamine)s (e.g., half-life 0.8 h for **4**). POE solubilizes salts such as $NOBF_4$ as the oxidizing agent and the desired cationic aminium radical in this paper by solvating cations with its ether residue, and has been often utilized in polymeric cation conductors.[10] The significant stability of the cationic diradical **2** in this paper is most likely caused by both the stilbene-linked structure to π-conjugatively couple the two diradicals with a sufficient distance and by the POE matrix to solvate the cationic sites.

The ESR spectrum of **1** at a low spin concentration gave a five-line signal at $g = 2.0026$, ascribed to the

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(8) Selected data for **1a**: MS (*m/e*) 739.1 (calcd), 739 (M^+); IR (KBr, cm^{-1}) δ 959 (C=C), ν 1322 (CN), ν 2961 (CH, Ph); δ_H (500 MHz, $CDCl_3$) 1.29 (s, 36H, *t*-Bu), 6.83−7.30 (m, 26H, aryl); δ_C (125 MHz, $CDCl_3$) 31.44, 31.46, 34.26, 34.28 (*t*-Bu), 119.82, 121.70, 122.61, 122.72, 123.70, 124.09, 125.99, 126.03, 126.60, 127.19, 128.36, 129.27, 130.72, 138.75, 144.84, 145.15, 145.41, 145.82, 147.69, 148.47 (CH).

(9) Selected data for **1b**: MS (*m/e*) 634.8 (calcd), 635 (M^+); IR (KBr, cm^{-1}) δ 963 (C=C), ν 1242 (COC), ν 1320 (CN); δ_H (500 MHz, $CDCl_3$) 1.29 (s, 12H, OCH_3), 6.77−7.26 (m, 26H, aryl); δ_C (125 MHz, $CDCl_3$) 55.48 (OCH_3), 114.65, 114.68, 118.46, 119.32, 120.06, 120.46, 126.17, 126.33, 126.57, 127.18, 128.25, 129.14, 129.59, 138.66, 140.76, 141.15, 148.22, 149.06, 155.66, 155.90 (CH).

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hyperfine coupling with two nitrogen nuclei (Figure 2a). The ESR spectrum changed to broad signals with increasing spin concentration, i.e., for **2**, due to a spin exchange, while no fine structure that gave the zero-field splitting parameters was detected. The $\Delta M_s = \pm 2$ forbidden transition ascribed to the triplet species was clearly observed for **2** at $g = 4$ in the frozen CH_2Cl_2 glass (Figure 2b). The signal intensity in the $\Delta M_s = \pm 2$ region was proportional to the reciprocal of the temperature ($1/T$) and followed Curie's law (Figure 2). This temperature dependence is consistent with **2** being a triplet ground-state diradical with a large triplet−singlet gap. (However, it does not rule out the possibility of a degenerate singlet/triplet state for **2**.)

The static magnetic susceptibility (χ) and magnetization (M) of **2** were measured using a SQUID magnetometer. Surprisingly, little attention has been devoted to such magnetic measurements on the cationic arylaminium radicals probably due to the instability of the radicals in the solid state. χ followed the Curie−Weiss law ($\chi = C/(T - \theta)$) for the powder sample of **2** embedded with diamagnetic POE, as shown in Figure 3 using the sample of **2b**. The Curie−Weiss behavior was reversible during repeated temperature depressions and elevations (1.8−300 K), which indicates the chemical stability of the diradical **2**. The Curie constant and Weiss constant (θ) were estimated by linear fitting to $1/\chi$ vs T plots, giving, e.g., 4.8×10^{-4} (emu K)/g and 2.0 K for **2b**.

The normalized plots of magnetization (M/M_s) for **2b** are close to the Brillouin curve for $S = {}^2/_2$ (Figure 3a),[11] indicating a triplet ground state for the diradical **2b**. The ratio of the effective magnetic moment (μ_{eff}) and the Bohr magneton (μ_B) was calculated from χ and the spin concentration (Figure 3b). The μ_{eff}/μ_B plots lie close to 2.83 (theoretical value for $S = {}^2/_2$) even at higher temperature. Curve fitting the μ_{eff}/μ_B vs T data to the Bleaney−Bowers expression[12] for a diradical system gave the parameters summarized in the caption of Figure 3. Stability of the triplet ground state ($\Delta E_{T-S} = 2J$) was estimated to be significantly large ($\gg kT$) for the diradical **2**. Compound **2** is classified as a nondisjointed diradical molecule and the nonbonding molecular orbitals of **2** effectively overlapped each other on the stilbene framework,[7,13] which could realize both the efficient spin-exchange interaction between the pendant spins and the stability of the diradical.

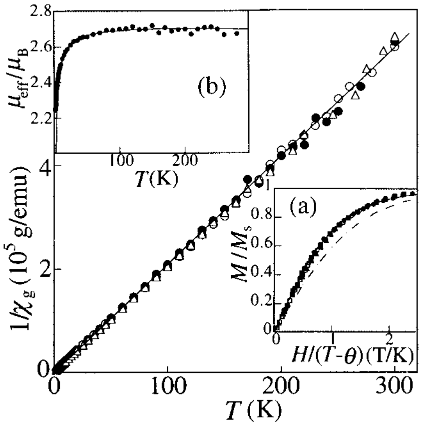

Figure 3. $1/\chi$ vs T plots with the Curie−Weiss fitting (solid line) of the powder sample of **2b** with spin concentration = 0.50 spin/N unit diluted with POE for temperature elevation (○), depression (●), and repeated elevation (△). Inset a: M/M_s vs $H/(T - \theta)$ plots of the **2b** sample at T = 1.8 (●), 2.0 (■), 2.25 (○), 5 (▲), 10 (□), and the theoretical curves corresponding to the $S = {}^1/_2$ and ${}^2/_2$ Brillouin functions. Inset b: μ_{eff}/μ_B vs T plots of the **2b** sample, and the simulation curve using the Bleany−Bowers expression (x_1 = 0.3, θ = −1.1 K, and $J \gg kT$).

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research (no. 09305060) from the Ministry of Education, Science and Culture, Japan, and by the NEDO Project on Technology for Novel High-Functional Materials.

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(11) The magnetization plots in Figure 3a were given by a self-consistent version of the mean field approximation.

(12) $\mu_{eff}/\mu_B = [6g^2T(1 - x_1)(T - \theta)^{-1}\{3 + \exp(-2J/kT)\}^{-1} + 3g^2Tx_1\{2(T - \theta)\}^{-1}]^{1/2}$. Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London* **1952**, *A214*, 451.

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