DOI: 10.1002/ejoc.200900403

Polycationic States of Oligoanilines Based on Wurster's Blue

Akihiro Ito,*[a] Daisuke Sakamaki,[a] Haruhiro Ino,[a] Aya Taniguchi,[a] Yasukazu Hirao,[a][‡]
Kazuyoshi Tanaka,*[a] Katsuichi Kanemoto,*[b] and Tatsuhisa Kato*[c]

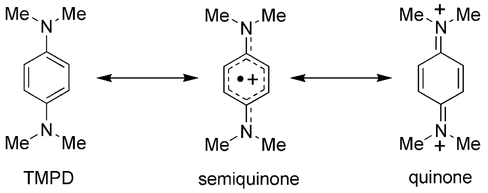
Keywords: Radical ions / Oxidation / Magnetic properties / Redox chemistry / EPR spectroscopy

Polycations of two oligoanilines based on Wurster's blue, *N*,*N*′,*N*′′-tris[4-(dimethylamino)phenyl]-*N*,*N*′,*N*′′-trimethyl-1,3,5-benzenetriamine (**2**) and *N*,*N*′-bis(3-{*N*-[4-(dimethylamino)phenyl]-*N*-methylamino}phenyl)-*N*,*N*′-dimethyl-*p*-phenylenediamine (**3**), have been generated efficiently by a stepwise oxidation procedure. Their redox behavior was characterized in terms of the embedded *p*-phenylenediamine (PD) units and their intramolecular connectivity. EPR analysis of the oxidized **2** and **3** species revealed the existence of high-spin species in solution. It was found that spin multiplicities of the dominant polycationic species of **2** and **3** formed by 3 equiv. of oxidant can be assigned to quartet and doublet states, respectively on the basis of pulsed EPR spectroscopy. These results demonstrate that the intramolecular connectivity between the spin-containing units decisively influences the spin preference of the multispin systems based on oligoanilines.

Introduction

The control of spin preference for multispin organic systems is of great importance in relation to their potential applications in molecular electronics such as novel spin-electronic devices. To achieve this control, many stable organic radical centers with desirable magnetic correlation should be assembled. Thus, many high-spin organic molecules containing several stable radical centers have been investigated to date.[1]

Wurster's blue radical cation ($TMPD^{\cdot+}$), which is generated by one-electron oxidation of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD), is one of the most chemically and thermally stable organic radicals and has long been investigated from different angles.[2] Its stability can be explained by π-electron delocalization in the semi-quinone structure (Scheme 1). However, the use of $TMPD^{\cdot+}$ as a spin-containing unit to exploit high-spin organic systems has not often been examined,[3–6] probably because the coupling reaction between aryl bromide and *N*-methylarylamine is not a feasible process. Recent progress in Pd-catalyzed C–N coupling reactions has facilitated the synthesis of various arylamines.[7,8]



Scheme 1. Wurster's blue (TMPD) and its related oxidation states.

We have already reported the magnetic properties of the oxidized species of TMPD-based compound **1** in which two TMPD radical cations are connected by 1,3-benzenediyl (Scheme 2).[4] Compound **1** was found to have three reversible redox states and the generated dication $\mathbf{1}^{2+}$ has a high-spin correlation. Furthermore, it has been suggested that the observed EPR spectrum of $\mathbf{1}^{2+}$ is the superposition of the spectra of several conformers that arise from the flexibility of the linear molecular structure. Moreover, very recently, Nelsen et al. found that the spin preference of the bis(radical cation) of a trimethylene-bridged cyclophane with two TMPD units depends on the conformations between two *p*-phenylenediamine (PD) units.[6] In this context, our attention was drawn to the extended oligomer models of TMPD-based high-spin polymers. In relation to TMPD-based high-spin oligomers, the polycationic states of the related *m*,*p*-arylamine oligomers have already been examined by Wienk and Janssen in detail.[9] In addition, Blackstock and co-workers have reported the electronic properties of

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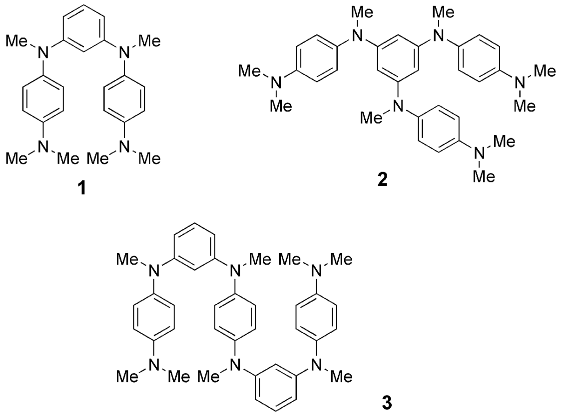
[a] Department of Molecular Engineering, Graduate School of Engineering, Kyoto University,
Nishikyo-ku, Kyoto 615-8501, Japan
E-mail: aito@scl.kyoto-u.ac.jp
a51053@sakura.kudpc.kyoto-u.ac.jp
[b] Department of Physics, Graduate School of Science, Osaka City University,
3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan
E-mail: kkane@sci.osaka-cu.ac.jp
[c] Department of Chemistry, Josai University,
1-1 Keyakidai, Sakado, Saitama 350-0295, Japan
E-mail: rik@josai.ac.jp
[‡] Present address: Department of Chemistry, Graduate School of Science, Osaka University,
1-1 Machikaneyamacho, Toyonaka, Osaka 560-0043, Japan

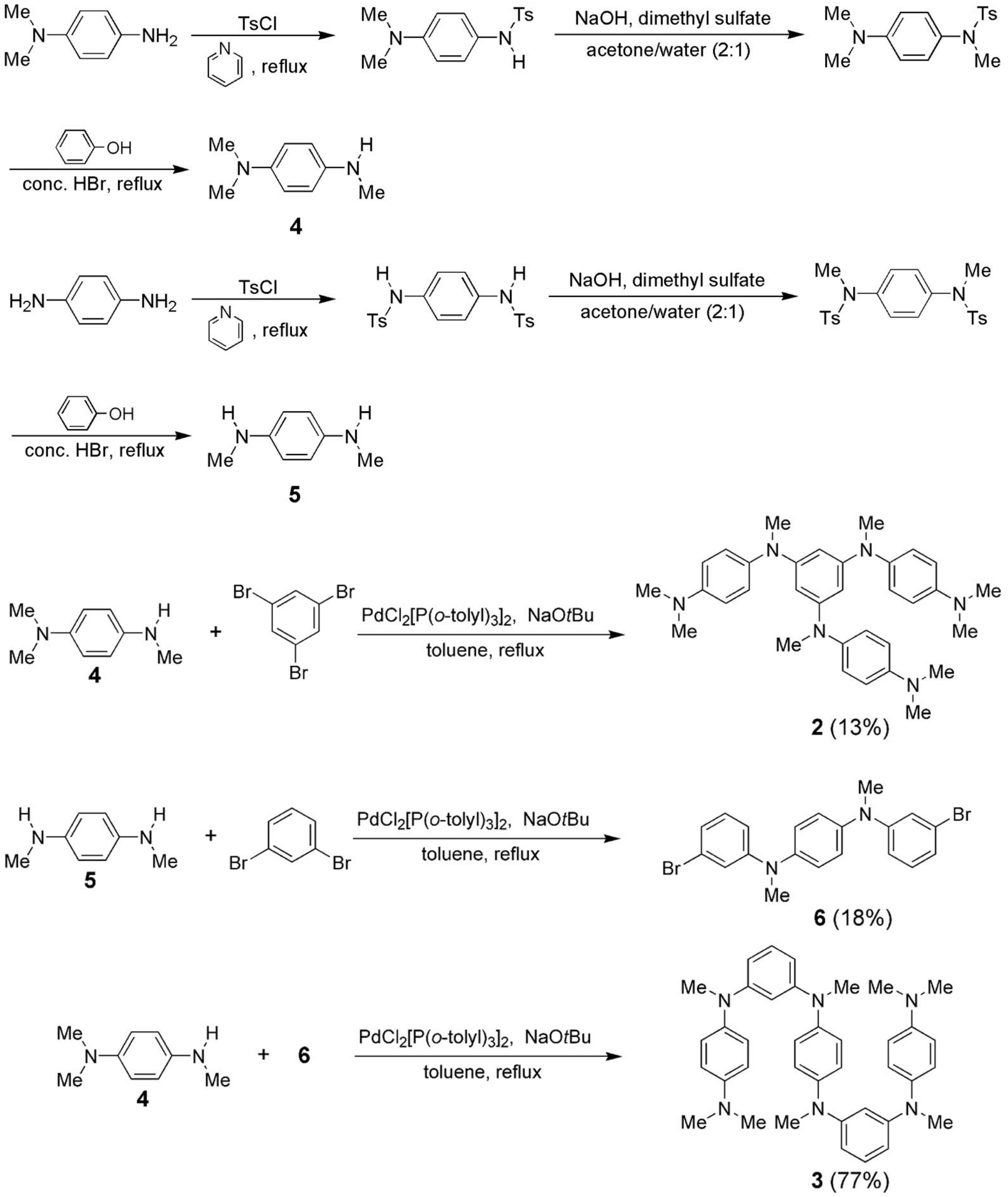
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200900403.

the radical cations of several types of dendritic PD-based oligoarylamines.[10] Furthermore, in recent years, a large number of new diaryl- and triarylamine oligomers have been synthesized and their physical properties examined.[11–27] Therefore, oligoarylamine-based molecular systems have attracted much attention from the viewpoint of molecular electronics.

Herein we report the electronic properties of the polycationic species of oligoanilines containing three TMPD units (**2** and **3**; Scheme 2). The *m*,*p*-aniline oligomer **3** has already been prepared to examine the spin multiplicity of the tri(radical cation) of **3**, but detailed characterization was not reported.[5] When three TMPDs are connected by a 1,3-benzenediyl or 1,3,5-benzenetriyl, the molecular structures are confined to two types: The two-dimensional dendritic



Scheme 2. TMPD-based oligoanilines **1**, **2**, and **3**.



Scheme 3. Synthesis of methylated *p*-phenylenediamines **4** and **5** and hexamines **2** and **3**.

form, like **2**, and the one-dimensional form, like **3**. In addition, the two isomers are expected to have a high-spin correlation in their tricationic states on the basis of a theoretical consideration of high-spin molecules.[28] However, these two isomers were found to differ considerably in their electrochemistry and, more importantly, in their spin preference because of the intramolecular connectivity of the TMPD units.

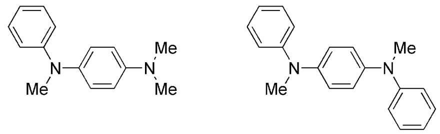
Results and Discussion

Synthesis

Compounds **2** and **3** were synthesized by following the procedure shown in Scheme 3. As the starting materials, we prepared various *N*-methyl-substituted *p*-phenylenediamines by *N*-tosylation, *N*-methylation with dimethyl sulfate, and detosylation. The key reaction in the synthesis of **2** and **3** is the Pd^0-catalyzed amination reaction, which was intensively investigated by Buchwald and co-workers[7] and Hartwig.[8] Compound **2** was synthesized from 1,3,5-tribromobenzene and tri-*N*-methylated PD (**4**) by utilizing [PdCl$_2${P(*o*-tolyl)$_3$}$_2$] as the catalyst.[29] Hexamine **3** was synthesized from di-*N*-methylated PD (**5**) by using successive catalytic amination reactions. The yield of **3** was found to be improved by our method in comparison with previously reported procedures.[5]

Redox Properties

First of all, understanding the redox behavior of **2** and **3** is indispensable for the investigation of their polycationic states. Hence we measured the cyclic voltammograms of **2** and **3** in MeCN solution at room temperature. The redox potentials of **2**, **3**, and their related arylamines (Scheme 4) are summarized in Table 1. As is evident from their cyclic voltammograms (Figure 1), compounds **2** and **3** show clear (quasi-)reversible multiredox behavior originating from the PD units.



PTMPD **DMDPPD**

Scheme 4.

Table 1. Redox potentials in MeCN versus Fc/Fc$^+$ (25 °C, 0.1 M nBu$_4$NClO$_4$, scan rate 100 mV/s).

Compound	E_1 [V]	E_2 [V]	E_3 [V]	E_4 [V]
TMPD	–0.29	+0.29		
PTMPD	–0.13	+0.38		
DMDPPD[a]	+0.05	+0.55		
1	–0.19	–0.01	+0.44[b]	
2	–0.23	–0.08	+0.06	+0.47[c]
3	–0.14[b]	+0.10	+0.43[b]	+0.56

[a] Measured in CH$_2$Cl$_2$ (see ref.[17]). [b] Quasi-two-electron oxidation. [c] Quasi-three-electron oxidation.

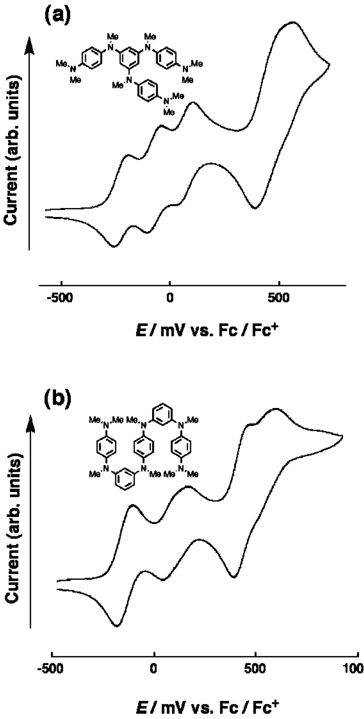


Figure 1. Cyclic voltammograms of (a) **2** and (b) **3** in MeCN at 298 K (scan rate 100 mV/s).

In the cyclic voltammogram of **2**, four redox states are observed [Figure 1 (a)]. Judging from the current ratio, the first three waves represent three single-electron oxidation processes and the fourth wave a three-electron oxidation process. The first three waves can be ascribed to the removal of one electron from each of the three PD units, comparable to the first oxidation potential of TMPD. The decrease in electron-donating ability can be attributed to the 1,3,5-benzenetriyl linker, as indicated by the decrease in the first oxidation potential of *N*-phenyl-*N*,*N*′,*N*′-trimethyl-*p*-phenylenediamine (PTMPD). The fact that the E_2–E_1 separation (0.15 V) is similar to that of E_3–E_2 (0.14 V) suggests that the electrostatic repulsion energy associated with stepwise oxidation increases additively with each electron removal. The three PD units were further oxidized at an oxidation potential of 0.47 V to generate the hexacation of **2**. Note that a three-electron oxidation simultaneously took place in **2**, whereas stepwise oxidation occurred in the related all-phenyl-substituted hexamine.[9]

On the other hand, the cyclic voltammogram of **3** in Figure 1 (b) reveals four redox couples. The current ratio for the first, second, third, and fourth waves was found to be 2:1:2:1, which indicates that the redox behavior of **3** consists of a two-electron oxidation (corresponding to the peripheral two PD units), a single-electron oxidation (corresponding to the central PD unit), a two-electron oxidation (corresponding to further oxidation of the two peripheral PD units), and a single-electron oxidation (corresponding to a further oxidation of the central PD units). This redox behavior is in accordance with that of the related all-phenyl-substituted hexamine.[9] Evidence corroborating that the first redox process is due to removal of an electron from the peripheral PD units is also given by the oxidation potential of –0.14 V. Namely, the first oxidation potential of **3** has a similar value to that of PTMPD, which indicates that the first oxidation process of **3** can be regarded as an independent removal of a single electron from two non-interacting PD units in order to reduce unfavorable electrostatic repulsions between the charged semi-quinoidal PD units. The removal of one electron from the central PD unit of **3** took place at a higher oxidation potential (+0.10 V) than the corresponding oxidation process of **2** (+0.06 V). What has to be noticed here is that the second oxidation potential of **3** has a larger value than the first oxidation potential (+0.05 V) of the compound related to the central PD unit of **3**, *N*,*N′*-dimethyl-*N*,*N′*-diphenyl-*p*-phenylenediamine (DMDPPD).[30] The reason for the decrease in the electron-donating ability of the central PD unit can, therefore, be derived from the electrostatic repulsion exerted by the charged peripheral PD units rather than from the electron-withdrawing effect of the substituted phenyl groups. Moreover, the oxidation from the trication to the hexacation was separated into two-electron and single-electron processes, unlike in **2**. This can probably be attributed to the fact that in $\mathbf{3}^{2+}$ the central PD unit is more positively charged than the peripheral PD units.

Spectroelectrochemical Studies

To elucidate the oxidized species generated during the oxidation of **2** and **3**, we recorded their optical absorption spectra in CH_2Cl_2 at room temperature using an optically transparent thin-layer electrochemical cell. As shown in Figure 2, the intervalence (IV) band originating from the PD units of **2** (and **3**) at about 600 nm increased upon oxidation of **2** (and **3**) to trication $\mathbf{2}^{3+}$ (and $\mathbf{3}^{3+}$), and the absorption band exhibited a vibrational fine structure, as is often observed for the semi-quinoidal radical cation of TMPD.[12h,31] This result is consistent with the fact that the π conjugation between the three PD units is segmented by ferromagnetic coupling units, 1,3,5-benzenetriyl for **2** and *m*-phenylene for **3**. Closer inspection of the near-IR region of the spectra recorded for the oxidation of $\mathbf{2}^{+}$ to $\mathbf{2}^{3+}$ revealed a weak IV charge transfer (IV-CT) band arising from the 1,3,5-benzenetriyl unit [Figure 2 (c)]. The intensity of the observed IV-CT band at about 920 nm decreased, with

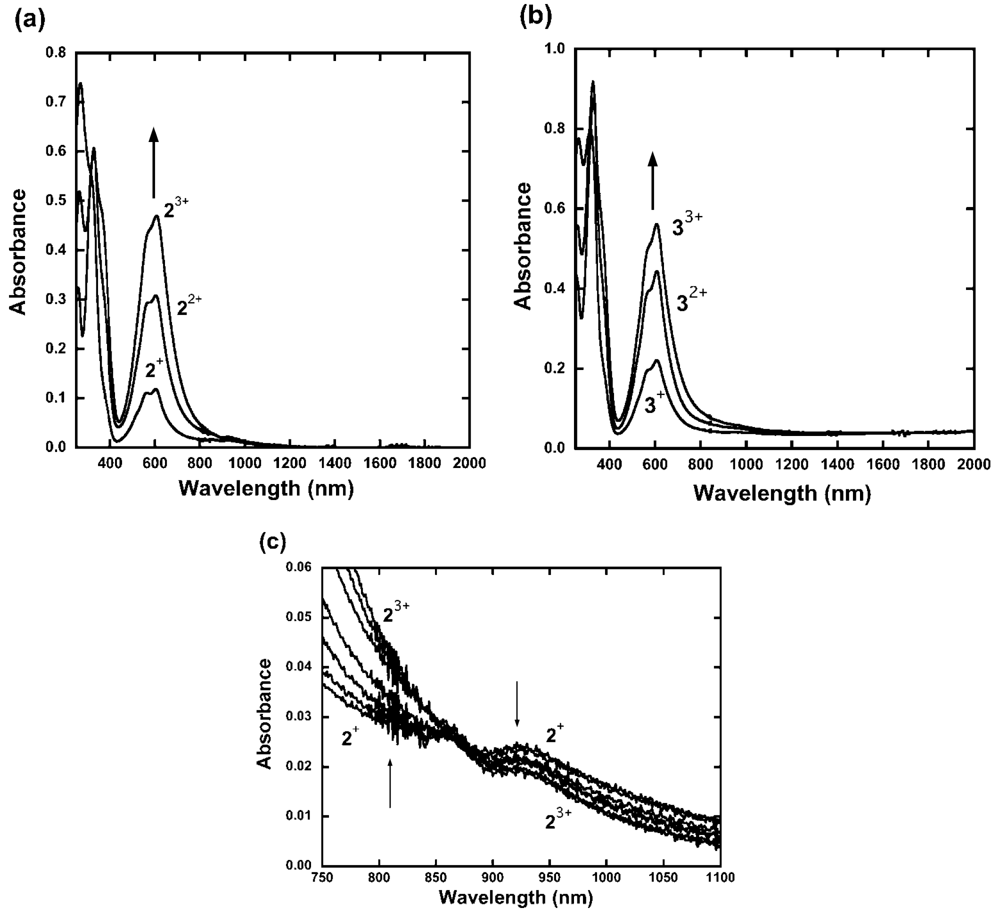


Figure 2. UV/Vis/NIR spectra recorded for the stepwise electrochemical oxidation of (a) **2** and (b) **3** in CH_2Cl_2/0.1 M nBu$_4$NBF$_4$ at room temperature. (c) Enlargement of the NIR region for the oxidation from $\mathbf{2}^{+}$ to $\mathbf{2}^{3+}$.

an isosbestic point at about 870 nm, during the oxidation from $\mathbf{2}^{+}$ to $\mathbf{2}^{3+}$. This strongly suggests that spin-hopping transfer takes place between the oxidized and neutral PD units in $\mathbf{2}^{+}$ and $\mathbf{2}^{2+}$.

CW-EPR Studies

As explained in the Introduction, when **2** and **3** are oxidized by 3 equiv. of oxidant, high-spin species with quartet spin multiplicity are expected to be dominant in solution. To check this, we chemically oxidized **2** and **3** by using tris(4-bromophenyl)aminium hexachloroantimonate ($\mathrm{TBA{\cdot}SbCl_6}$)[32] as the oxidant. Judging from the high oxidation potential of TBA (ca. 0.84 V vs. $\mathrm{Fc/Fc^+}$ in MeCN at room temperature), the added oxidant was completely consumed in the oxidation of **2** and **3** in solution. Treatment of **2** (1 mM) with up to 1 mol-equiv. of $\mathrm{TBA}^{\cdot+}$ in *n*-butyronitrile at 203 K yielded a dark bluish-green solution, which showed a single-line EPR spectrum with no detectable fine structure at 123 K. However, on treatment with 2–3 equiv. of $\mathrm{TBA}^{\cdot+}$, the EPR spectrum began to show shoulders in addition to the main spectrum in the $\Delta M_S = \pm 1$ region. Moreover, the forbidden $\Delta M_S = \pm 2$ resonance at half-field was observed. This forbidden resonance indicates the existence of high-spin species with spin multiplicity larger than a triplet.[33] When the solution was cooled to 5 K, we also detected the forbidden $\Delta M_S = \pm 3$ resonance at one-third field, as shown in Figure 3 (a). Generally speaking, it is difficult to observe the forbidden $\Delta M_S = \pm 3$ resonance.[34] Hence, this provides unequivocal evidence for the existence of quartet spin species $\mathbf{2}^{3+}$.[35] Upon further one-electron oxidation, the forbidden resonance signal faded away, and finally the EPR spectrum revealed only traces of doublet species, which essentially indicates the decomposition of further oxidized species.

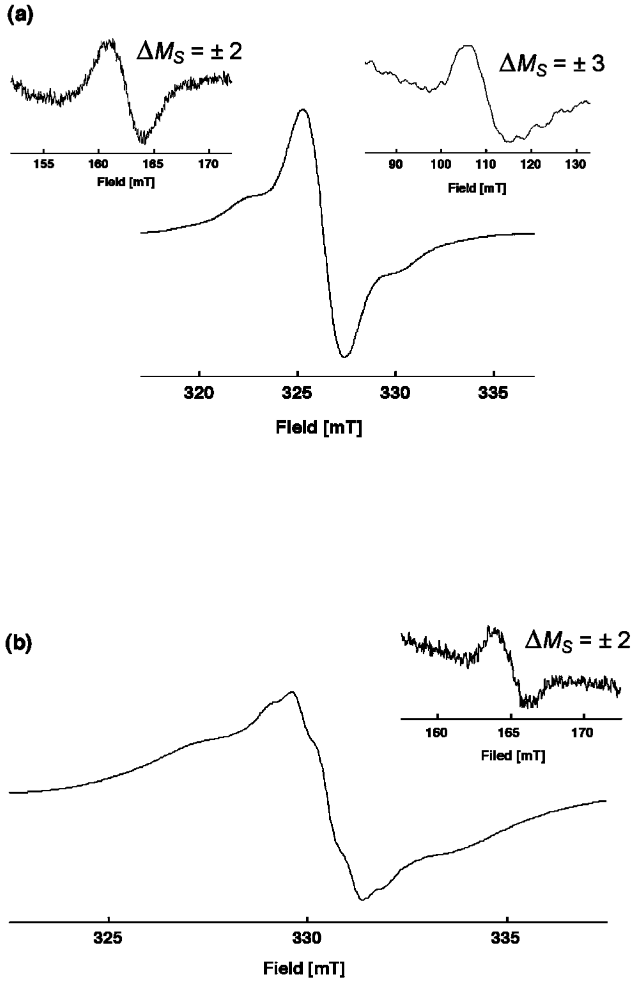


Figure 3. EPR spectra of (a) **2** oxidized by 3 mol-equiv. of $\mathrm{TBA{\cdot}SbCl_6}$ in *n*-butyronitrile at 5 K [insets: the forbidden $\Delta M_S = \pm 2$ and $\Delta M_S = \pm 3$ resonances at 5 K] and (b) **3** oxidized by 3 mol-equiv. of $\mathrm{TBA{\cdot}SbCl_6}$ in *n*-butyronitrile at 123 K [inset: the forbidden $\Delta M_S = \pm 2$ resonance at 123 K].

On the other hand, in the EPR spectra of the oxidized species of **3** treated with up to 2 mol-equiv. of $\mathrm{TBA{\cdot}SbCl_6}$ in *n*-butyronitrile at 203 K, no detectable fine-structured spectrum was observed at 123 K. As described in the previous section, this is consistent with the fact that the first two-electron oxidation of **3** has been ascribed to the oxidation of the two peripheral PD units because the separation of the two peripheral oxidized PD units leads to weak magnetic dipole–dipole interactions.[33] Three-electron oxidation of **3** at 203 K with 3 mol-equiv. of $\mathrm{TBA{\cdot}SbCl_6}$ gave a partially fine-structured EPR spectrum [Figure 3 (b)]. The forbidden $\Delta M_S = \pm 3$ resonance was not detected, but the forbidden $\Delta M_S = \pm 2$ resonance was observed at about 165 mT.

Pulsed EPR Studies

In the preceding section, various differences in the EPR spectra of the oxidized species of **2** and **3** were observed depending on the quantity of added oxidant. To identify unequivocally the spin multiplicity of the major species at each oxidation stage, we carried out experiments using one of the pulsed EPR methods, ESTN (the electron-spin transient nutation method). The ESTN method is based on the fact that magnetic moments with distinct spin quantum number S precess with a specific nutation frequency ω_{nut} in the presence of a microwave irradiation field B_1 and a static magnetic field B.[36] If the microwave irradiation field ($\omega_1 = -\gamma_{\mathrm{e}} B_1$; γ_{e} is the gyromagnetic ratio of the electron) is weak enough compared with the fine-structure parameter, the nutation frequency for the $|S, M_S\rangle \leftrightarrow |S, M_S + 1\rangle$-allowed transition is represented to a good approximation by Equation (1). This equation indicates that the nutation frequency ω_{nut} can be scaled with the spin quantum numbers S and M_S with a unit of ω_1, the nutation frequency for the spin doublet state [$\omega_1 = \omega_{\mathrm{doublet}}$].[36,37]

$$\omega_{\mathrm{nut}} = [S(S+1) - M_S(M_S+1)]^{\frac{1}{2}\omega_1} \qquad (1)$$

The relation between the echo-detected field-swept EPR spectra observed at 5 K and its transient nutation (TN) spectra is depicted in a 2D contour representation in Figure 4. The projection along the magnetic field axis roughly corresponds to the usual CW-EPR spectrum, whereas the projection along the frequency axis corresponds to the TN spectrum. The three spectra in Figure 4 were obtained when 2–4 equiv. of oxidant were added to the *n*-butyronitrile solution of **2**. As shown in Figure 4, the nutation frequency (32.0 MHz) observed at the central field (343.2 mT) can be ascribed to the $|\frac{1}{2}, +\frac{1}{2}\rangle \leftrightarrow |\frac{1}{2}, -\frac{1}{2}\rangle$ transition of the doublet $\mathbf{2}^{+}$ ($\omega_1 = \omega_{\text{doublet}}$), judging from the microwave power dependence of the nutation frequency.

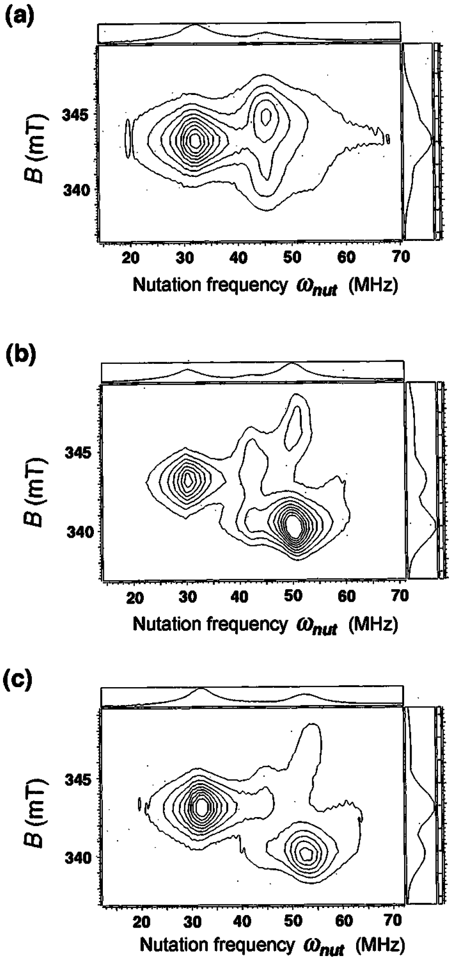


Figure 4. Field-swept electron-spin transient nutation spectra of **2** oxidized by (a) 2, (b) 3, and (c) 4 mol-equiv. of TBA·SbCl$_6$ in *n*-butyronitrile at 5 K. ω_1 (= ω_{doublet}) corresponds to about 32 MHz.

For the sample treated with 2 equiv. of oxidant, a new intense peak at 344.8 mT appeared with a nutation frequency of 45.2 MHz, which suggests the generation of a high-spin cationic species of **2** [Figure 4 (a)]. Here, the frequency ratio ($\omega_{\text{nut}}/\omega_{\text{doublet}}$) of 1.41 is in good agreement with the ratio of $\sqrt{2}$ expected for the $|1, 0\rangle \leftrightarrow |1, \pm1\rangle$ transition of a triplet state from Equation (1). As a result, the triplet species generated can be regarded as $\mathbf{2}^{2+}$. In addition, a shoulder peak at 341.6 mT with the same nutation frequency can be observed [Figure 3 (a)]. This corresponds to the $\Delta M_S = \pm1$ resonance for triplet $\mathbf{2}^{2+}$ at a lower field, which suggests asymmetry of the EPR spectrum of the triplet $\mathbf{2}^{2+}$. After oxidation of **2** with 3 equiv. of oxidant, the TN spectrum clearly shows two new peaks at 340.2 and 346.0 mT with a nutation frequency of 50.2 MH [Figure 4 (b)]. The ratio between 50.2 and 32.0 MHz was estimated to be 1.57, a value close to $\sqrt{3}$. On the basis of Equation (1), the two peaks at 340.2 and 346.0 mT have been assigned to $|\frac{3}{2}, \pm\rangle \leftrightarrow |\frac{3}{2}, \pm\frac{1}{2}\rangle$ transitions of the quartet state of $\mathbf{2}^{3+}$. The nutation signal corresponding to the $|\frac{3}{2}, \frac{1}{2}\rangle \leftrightarrow |\frac{3}{2}, -\frac{1}{2}\rangle$ transition was not observed for this sample. Note that the resonance of $\mathbf{2}^{3+}$ at a lower field has a stronger intensity than that at a higher field, whereas the resonance of $\mathbf{2}^{2+}$ at a higher field has a stronger intensity than that at a lower field. The reason why the nutation spectra of $\mathbf{2}^{2+}$ and $\mathbf{2}^{3+}$ are asymmetric is unclear at this stage. When more oxidant was added, the amount of $\mathbf{2}^{3+}$ decreased gradually [Figure 4 (c)].

On the other hand, as shown in Figure 5 (a), the nutation frequency (34.3 MHz) observed at the central field (342.4 mT) has been ascribed to the $|\frac{1}{2}, +\frac{1}{2}\rangle \leftrightarrow |\frac{1}{2}, -\frac{1}{2}\rangle$ transition of the doublet $\mathbf{3}^{+}$, similarly to compound **2**. Unlike **2**, however, the high-spin component in oxidized species of **3** was not dominant in solution. As shown in Figure 5 (b), the TN spectrum of **3** treated with 3 equiv. of oxidant revealed only a trace of the nutation signal attributable to quartet spin multiplicity (ca. 50 MHz) except for the dominant doublet spin signal (ca. 34 MHz). Even at elevated temperatures (ca. 80 K), an increase in intensity was not observed, which indicates a small fraction of quartet spin species of $\mathbf{3}^{3+}$ in solution. This observation supports the recent report by Kulszewicz–Bajer et al.[15b] who showed that the polycationic state of the simplest linear alternating *m,p*-polyaniline results in the mainly uncoupled ($S = \frac{1}{2}$)

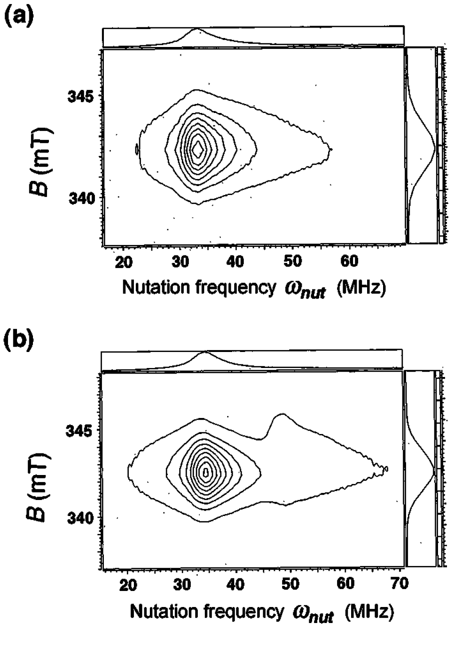


Figure 5. Field-swept electron-spin transient nutation spectra of **3** oxidized by (a) 1 and (b) 3 mol-equiv. of TBA·SbCl$_6$ in *n*-butyronitrile at 5 K. ω_1 (= ω_{doublet}) corresponds to about 34 MHz.

spin system. Hence, these results for linear hexamine **3** strongly suggest difficulty in realizing the high-spin linear alternating *m*,*p*-polyaniline.

Conclusions

We have reported the results of the synthesis and magnetic properties of extended oligomer models of TMPD-based high-spin polymers **2** and **3**. These two compounds display clear multistage redox behavior. In **2**, each PD unit can be oxidized successively into the trication $\mathbf{2}^{3+}$. On the other hand, the two peripheral PD units of **3** were simultaneously oxidized at the first oxidation potential and then single-electron removal from the central PD unit gave rise to the trication $\mathbf{3}^{3+}$. The EPR spectra of the species oxidized by 3 equiv. of the oxidant showed that the high-spin components were generated in solution, judging from the observation of the forbidden resonance. In particular, for **2**, the $\Delta M_S = \pm 3$ resonance was clearly detected, which indicates the existence of the quartet $\mathbf{2}^{3+}$. Moreover, when the two isomers were treated with 3 equiv. of the oxidant, pulsed EPR spectroscopy revealed that the quartet $\mathbf{2}^{3+}$ was the dominant species in solution, whereas the quartet $\mathbf{3}^{3+}$ was barely observed. We have therefore succeeded in elucidating the influence of the connectivity between the spin-containing units (i.e. semi-quinoidal PD units) on the retention of high-spin alignment.

Experimental Section

General: Commercial grade reagents were used without further purification. Solvents were purified, dried, and degassed following standard procedures. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL EX-270KS (400 MHz) spectrometer. Chemical shifts are given in parts per million (δ) relative to tetramethylsilane (TMS) as the internal standard. High-resolution mass spectra were obtained with a JEOL JMS-700 spectrometer. Melting points were measured with a Yanaco micro-melting point apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Center, Kyoto University.

Physical Measurements: Cyclic voltammetry (CV) measurements were taken with 0.1 M $n\mathrm{Bu_4NClO_4}$ in MeCN (25 °C, scan rate 100 mV/s) using a BAS CV-50W voltammetric analyzer with a three-electrode cell using a Pt disk (2 mm^2) and a Pt wire as the working and counter electrodes, respectively, and Ag/0.01 M $\mathrm{AgNO_3}$ (MeCN) as the reference electrode. EPR spectra were recorded with JEOL JES-RE-2X and JES-TE-200 X-band spectrometers. The temperature was controlled with a JEOL DVT2 variable-temperature unit in the range 120–180 K and with an Oxford ITC-503 temperature controller combined with an EPR-910 continuous flow cryostat in the range 4–100 K. Pulsed EPR experiments were performed with a Bruker ELEXSYS E580 X-band FT EPR spectrometer. The microwave pulse power of 10 mW provided by the microwave bridge was boosted to 1 kW by using a traveling wave tube (TWT) amplifier. The microwave field amplitude of the sample was approximately 0.5 mT, as determined by the $\pi/2$ pulse length of 16 ns. The pulse width of the detection sequence was 4 and 8 ns because of optimizing the detection of a spin state greater than $S = 1$. The microwave pulse sequence used in this study is similar to that reported previously.[12j] For the transient nutation experiment, the two-pulse electron spin echo signal $S(t_1)$ was detected by increasing the width (t_1) of the nutation pulse. We employed appropriate phase cycles to suppress undesirable signals and artifacts that arise from an inaccurate pulse length.[38,39] The observed signal $S(t_1, B)$ as a function of the external magnetic field B was converted into a nutation frequency domain $S(\omega_\mathrm{nut}, B)$ spectrum by Fourier transformation along the t_1 direction.

***N*,*N*,*N*′-Trimethyl-*p*-phenylenediamine (4):** A mixture of *N*,*N*-dimethyl-*p*-phenylenediamine (26.1 g, 0.192 mol) and tosyl chloride (36.6 g, 0.192 mol) in pyridine (90 mL) was heated at reflux and stirred for 1 h. After being cooled to room temperature, ice-cold water was added to the reaction mixture. After filtration and washing with water, a gray tosylated product was obtained quantitatively. Dimethyl sulfate (32 mL, 0.337 mol) was added dropwise to a solution of the tosylate (55.7 g, 0.192 mol) and NaOH (15.0 g, 0.375 mol) in acetone/water (2:1) with stirring. After stirring for 6 h, the reaction mixture was filtered. The resulting green solid was washed with water (33.1 g, 56.7%). Finally, a mixture of the obtained *N*′-tosyl-*N*,*N*,*N*′-trimethyl-*p*-phenylenediamine (20.0 g, 0.066 mol) and phenol in concd. HBr (100 mL) was heated at reflux and stirred for 1 h. After being cooled to room temperature, the reaction mixture was washed with $\mathrm{Et_2O}$. NaOH was added to the aqueous layer until the solution was alkaline. Liberated amine was taken up with $\mathrm{Et_2O}$. The organic layer was dried with $\mathrm{MgSO_4}$ and evaporated to furnish **4** as a dark-red liquid (5.27 g, 53.4%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ = 2.73 (s, 3 H, NC*H*$_3$), 2.78 (s, 6 H, NC*H*$_3$), 3.27 (br. s, 1 H, N*H*), 6.56 (m, 2 H, *p*-Ph*H*-3), 6.73 (m, 2 H, *p*-Ph*H*-2) ppm. ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ = 31.65 (NH*C*H$_3$), 42.30 [N(*C*H$_3$)$_2$], 113.74 (C-3), 115.85 (C-2), 141.88 (C-4), 143.94 (C-1) ppm. $\mathrm{C_9H_{14}N_2}$ (150.22): calcd. C 71.96, H 9.39, N 18.65; found C 72.02, H 9.28, N 18.53.

***N*,*N*′-Dimethyl-*p*-phenylenediamine (5):** A mixture of *p*-phenylenediamine (12.4 g, 0.114 mol) and tosyl chloride (43.7 g, 0.229 mol) in pyridine (120 mL) was heated at reflux and stirred for 2 h. After being cooled to room temperature, ice-cold water was added to the reaction mixture. After filtration and washing with water, a purple ditosylated product was obtained quantitatively. Dimethyl sulfate (52.8 mL, 0.557 mol) was added dropwise with stirring to a suspension of the ditosylate (47.7 g, 0.114 mol) and NaOH (22.4 g, 0.559 mol) in acetone/water (2:1). After stirring for 18 h, the reaction mixture was filtered. The resulting pink solid was washed with water (47.3 g, 93.0%). Finally, a mixture of the obtained *N*,*N*′-ditosyl-*N*,*N*′-dimethyl-*p*-phenylenediamine (5.0 g, 0.011 mol) and phenol (10 g, 0.11 mol) in concd. HBr (50 mL) was heated at reflux and stirred for 1 h. After being cooled to room temperature, the reaction mixture was washed with $\mathrm{Et_2O}$. NaOH was added to the aqueous layer until the solution was alkaline. Liberated amine was taken up with $\mathrm{Et_2O}$. The organic layer was dried with $\mathrm{Na_2SO_4}$ and evaporated to afford **5** as a red solid (1.20 g, 78.4%); m.p. 52.0–52.5 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ = 2.78 (s, 6 H, NC*H*$_3$), 3.20 (br. s, 2 H, N*H*), 6.57 (s, 4 H, *p*-PhH-2, *p*-PhH-3) ppm. ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ = 31.9 (NH*C*H$_3$), 114.26 (C-2), 141.87 (C-1) ppm. $\mathrm{C_8H_{12}N_2}$ (136.20): calcd. C 70.55, H 8.88, N 20.57; found C 70.78, H 8.74, N 20.46.

***N*,*N*′,*N*′′-Tris[4-(dimethylamino)phenyl]-*N*,*N*′,*N*′′-trimethyl-1,3,5-benzenetriamine (2):** A mixture of **4** (1.42 g, 9.45 mmol), 1,3,5-tribromobenzene (0.74 g, 2.4 mmol), sodium *tert*-butoxide (1.09 g, 11.3 mmol), and $[\mathrm{PdCl_2\{P(\mathit{o}\text{-tolyl})_3\}_2}]$ (0.078 g, 0.10 mmol) in toluene was heated under nitrogen at 110 °C for 18 h. After being cooled to room temperature, the reaction mixture was taken up with $\mathrm{Et_2O}$ and washed with brine. The organic layer was dried with

MgSO$_4$. After evaporation of the solvent, purification by column chromatography on silica gel using AcOEt/*n*-hexane (2:1) gave doubly aminated **1** (0.27 g, 31%) and triply aminated **2** (0.16 g, 13%); m.p. 192 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.89 [s, 18 H, N(CH_3)$_2$], 3.10 [s, 9 H, N(CH_3)], 5.78 (s, 3 H, H$_A$), 6.67 (d, ^3J = 8.8 Hz, 6 H, H$_B$-2), 7.01 (d, ^3J = 8.8 Hz, 6 H, H$_B$-3) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 40.5 (NCH$_3$), 41.3 [N(CH$_3$)$_2$], 96.6 (C$_A$-2), 113.8 (C$_B$-3), 125.1 (C$_B$-2), 139.6 (C$_B$-1), 147.0 (C$_B$-4), 150.9 (C$_A$-1) ppm. $C_{33}H_{42}N_6$ (522.74): calcd. C 75.82, H 8.10, N 16.08; found C 75.70, H 8.13, N 15.80.

***N,N′*-Bis(3-bromophenyl)-*N,N′*-dimethyl-*p*-phenylenediamine (6):** A mixture of **5** (1.02 g, 7.00 mmol), 1,3-dibromobenzene (8.85 g, 38.0 mmol), sodium *tert*-butoxide (1.80 g, 19.0 mmol), and [PdCl$_2${P(*o*-tolyl)$_3$}$_2$] (0.20 g, 0.25 mmol) in toluene (25 mL) was heated under nitrogen at 100 °C for 6 h. After being cooled to room temperature, the reaction mixture was taken up with Et$_2$O and washed with brine. The organic layer was dried with Na$_2$SO$_4$. After evaporation of the solvent, purification by column chromatography on silica gel using CH$_2$Cl$_2$/*n*-hexane (1:2) afforded **6** (0.60 g, 18%); m.p. 172.5–173.5 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.28 (s, 6 H, NCH_3), 6.80 (ddd, ^3J = 8.30, ^4J = 2.44, 0.98 Hz, 2 H, H$_B$-6), 6.95 (ddd, ^3J = 7.81, ^4J = 1.71, 0.98 Hz, 2 H, H$_B$-4), 7.03 (t, ^4J = 2.20 Hz, 2 H, C$_B$-2), 7.06 (s, 4 H, H$_A$), 7.07 (t, ^3J = 8.05 Hz, 2 H, C$_B$-5) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 40.4 (NCH$_3$), 115.8 (C$_B$-6), 119.8 (C$_B$-2), 122.2 (C$_B$-4), 123.1 (C$_B$-3), 124.7 (C$_A$-2), 130.2 (C$_B$-5), 143.9 (C$_A$-1), 150.4 (C$_B$-1) ppm. $C_{20}H_{18}Br_2N_2$ (446.18): calcd. C 53.84, H 4.07, N 6.28, Br 35.82; found C 54.09, H 4.07, N 6.18, Br 35.72.

***N,N′*-Bis(3-{*N*-[4-(dimethylamino)phenyl]-*N*-methylamino}phenyl)-*N,N′*-dimethyl-*p*-phenylenediamine (3):** A mixture of **4** (1.15 g, 7.66 mmol), **6** (0.30 g, 0.67 mmol), sodium *tert*-butoxide (0.18 g, 1.87 mmol), and [PdCl$_2${P(*o*-tolyl)$_3$}$_2$] (0.02 g, 0.025 mmol) in toluene (10 mL) was heated under nitrogen at 100 °C for 21 h. After being cooled to room temperature, the reaction mixture was taken up with Et$_2$O and washed with brine. The organic layer was dried with Na$_2$SO$_4$. After evaporation of the solvent, purification by column chromatography on silica gel using AcOEt/*n*-hexane (1:4) afforded **3** (0.30 g, 77%); m.p. 180.0–180.5 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.92 [s, 12 H, N(CH_3)$_2$], 3.20 (s, 6 H, NCH_3), 3.22 (s, 6 H, NCH_3), 6.28 (dd, ^3J = 8.05, ^4J = 2.2 Hz, 2 H, H$_B$-4 or H$_B$-6), 6.32 (dd, ^3J = 8.05, ^4J = 2.2 Hz, 2 H, H$_B$-4 or H$_B$-6), 6.38 (t, ^4J = 2.2 Hz, 2 H, H$_B$-2), 6.72 (d, ^3J = 9.03 Hz, 4 H, H$_C$-2), 6.96 (s, 4 H, H$_A$), 7.01 (t, ^3J = 8.05 Hz, 2 H, H$_B$-5), 7.04 (d, ^3J = 9.03 Hz, 4 H, H$_C$-3) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 40.3 (NCH$_3$), 40.4 (NCH$_3$), 41.0 [N(CH$_3$)$_2$], 105.4 (C$_B$-2 or C$_B$-4 or C$_B$-6), 107.4 (C$_B$-2 or C$_B$-4 or C$_B$-6), 108.6 (C$_B$-2 or C$_B$-4 or C$_B$-6), 113.5 (C$_C$-2), 122.5 (C$_A$-3), 126.3 (C$_C$-2), 129.0 (C$_B$-5), 138.7 (C$_A$-1 or C$_C$-1 or C$_C$-4), 143.4 (C$_A$-1 or C$_C$-1 or C$_C$-4), 147.6 (C$_A$-1 or C$_C$-1 or C$_C$-4), 150.0 (C$_B$-1 or C$_B$-3), 150.7 (C$_B$-1 or C$_B$-3) ppm. HRMS (EI$^+$): calcd. for $C_{38}H_{44}N_6$ [M]$^+$: 584.3627; found 584.3614.

***N*-Phenyl-*N,N′,N′*-trimethyl-*p*-phenylenediamine (PTMPD):** A mixture of **4** (2.86 g, 19.0 mmol), bromobenzene (2.39 g, 15.0 mmol), sodium *tert*-butoxide (2.13 g, 22.0 mmol), and [PdCl$_2${P(*o*-tolyl)$_3$}$_2$] (0.36 g, 0.46 mmol) in toluene (20 mL) was heated under nitrogen at 100 °C for 6 h. After being cooled to room temperature, the reaction mixture was taken up with Et$_2$O and washed with brine. The organic layer was dried with MgSO$_4$. After evaporation of the solvent, purification by column chromatography on silica gel using AcOEt/*n*-hexane (1:3) afforded PTMPD (1.65 g, 47.9%) as a dark-green solid; m.p. 56.5–57.0 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.85 [s, 6 H, N(CH_3)$_2$], 3.18 (s, 3 H, NCH_3), 6.66–6.73 (m, 5 H, *N*-Ph-*H*, *p*-Ph-*H*), 7.01–7.04 (m, 2 H, *N*-Ph-*H*, *p*-Ph-*H*), 7.09–7.15 (m, 2 H, *N*-Ph-*H*, *p*-Ph-*H*) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 40.4 (NCH$_3$), 40.9 [N(CH$_3$)$_2$], 113.7 [C-2 (*p*-Ph) or C-2 or C-4 (*N*-Ph)], 114.6 [C-2 (*p*-Ph) or C-2 or C-4 (*N*-Ph)], 117.4 [C-2 (*p*-Ph) or C-2 or C-4 (*N*-Ph)], 126.8 [C-3 (*p*-Ph)], 128.8 [C-3 (*N*-Ph)], 138.7 [C-1 or C-4 (*p*-Ph)], 148.0 [C-1 or C-4 (*p*-Ph)], 150.0 [C-1 (*N*-Ph)] ppm. $C_{15}H_{18}N_2$ (226.32): calcd. C 79.61, H 8.02, N 12.38; found C 79.76, H 8.03, N 12.26.

Supporting Information (see also the footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of compounds **2**–**6** and **PTMPD**.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS) (B 20350065). Thanks are due to the Research Center for Molecular-Scale Nanoscience at the Institute for Molecular Science for the use of the pulsed EPR spectrometer.

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Received: April 13, 2009