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Synthesis of 1,3-Bis(diarylamino)benzenes as Model Precursors for One-Dimensional Organic Ferromagnetic Metals; Characterization of the Di-cations by Cyclic Voltammetry and Electron Spin Transient Nutation Spectroscopy

Masafumi Yano[†], Kazunobu Sato[†], Daisuke Shiomi[††], Akio Ichimura[†]
Kyo Abe[†*], Takeji Takui[†*], and Koichi Itoh[††*]

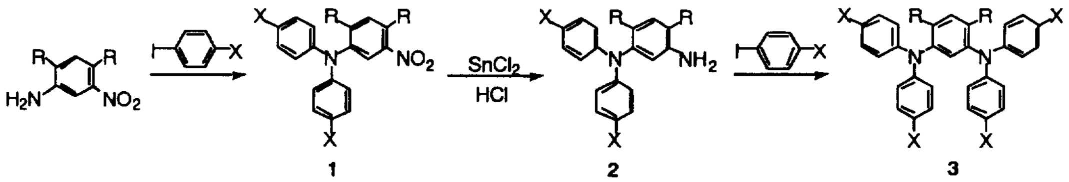
Department of Chemistry[†] and Department of Material Science[††]
Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558, Japan

***Abstract*:** A series of 1,3-bis(diarylamino)benzenes as model precursors for 1D organic ferromagnetic metals were synthesized. Cyclic voltammetric measurements showed that the corresponding mono- and dication radicals with protecting groups were stable enough even at ambient temperature. A triplet state for the dication was unequivocally identified by a novel electron spin transient nutation spectroscopy.

During the last decade, development of spin manipulation in chemistry underlying molecule-based magnetism has given rise to diverse topics in the pure and applied sciences. Among these, charged organic high-spin systems of elaborate molecular designs based on through-bond topological symmetry have emerged as models for charge fluctuation vs. spin polarization, *i.e.*, model compounds for organic ferromagnetic metals.[1] Since *para*-substituted triphenylaminium cations are known to be persistent radicals, *meta*-linked polycationic diarylaminobenzenes are promising as positively charged stable high-spin molecules. So far, attempts to synthesize and characterize *meta*-linked poly- or oligoarylaminobenzenes have been made by several groups.[2] Recently, Blackstock *et al.* have reported mono-, di-, and trication of 1,3,5-tris(diarylamino)benzenes, which are stable at low temperature (<-40℃).[2f,g]

Here we report the synthesis of a series of 1,3-bis(diarylamino)benzenes, which can be thought as the most basic precursors for positively charged high-spin molecules. Cyclic voltammetry (CV) and Electron Spin Transient Nutation (ESTN) spectroscopy were invoked in order to characterize their chemical stability and electronic spin structure, respectively. Their molecular design is based on the use of topologically controlled pseudo degeneracy of π-bonding MO's (π-topological pseudo degeneracy). Oxidation of these precursors are expected to yield polycationic high-spin heteroatomic systems because of the pseudo degeneracy due to the topology of π-conjugation in heteroatomic systems.

A series of 1,3-bis(diarylamino)benzenes(**3**) were synthesized as shown in Scheme 1 (see Table 1 for R and X). Using the Ullmann reaction, mixtures of *m*-nitroanilines and *p*-substituted iodobenzenes(4.5eq.) in *o*-dichlorobenzene were heated in the presence of Cu/K_2CO_3 at 180℃ for 12h to afford *m*-nitrotriphenylamines (**1**) in 20-70% yield. After reduction of **1** with $SnCl_2$/HCl in ethanol (yield 80-90%), second Ullmann reactions of the resultant diamines(**2**) with *p*-substituted iodobenzenes were carried out and the obtained crude products were purified with column-chromatography (silica gel, $CHCl_3$) to afford **3** in moderate yield (typically 10-20%).[3] Unfortunately, Ullmann coupling of *m*-dibromobenzenes and diphenylamines gave complex mixtures which we failed to purify.



Scheme 1

Table 1. A Series of **3** Synthesized

	R	X
3a	H	C_2H_5
3b	H	CH_3
3c	H	H
3d	H	F
3e	H	Cl
3f	CH_3	OCH_3
3g	CH_3	CH_3
3h	CH_3	H

Redox potentials of **3** were obtained using CV measurements. For **3a-e**, only the first oxidation peak was observed and the corresponding reduction wave could not be observed even at -78℃ with a scan rate of 100mV/s. The first oxidation peak potentials (E_{ox1}) reflect the effectiveness of *p*-substituents on the four outer phenyl rings. The E_{ox1}'s for **3a-e** are summarized in Table 2.

Table 2. Peak Potentials for the First Oxidation Process of **3a-e** and **3h** in n-PrCN(0.1M-Bu_4NPF_6 at -78℃)[a].

3	**3a**	**3b**	**3c**	**3d**	**3e**	**3h**
E_{ox1}(mV)	559	573	699	765	802	694

a) Potentials are on vs. a Ag/Ag^+ relative electrode with a scan rate of 100mV/s.

In contrast, for **3f** and **3g**, chemical stability of the corresponding cations is remarkably enhanced. Even at ambient temperature, two reversible redox couples ($I_{red}/I_{ox} \fallingdotseq 1$) both for **3f** and **3g** are observed as seen in Fig. 1, showing the effective control of *p*- and *o*-methyl substitution in the central ring to increase their chemical stability. $\Delta E_p = |E_{ox} - E_{red}|$ for the first and second redox couple for **3f** and **3g** are 79 and 74mV, 62 and 65mV, respectively (see Table 3). No additional oxidation wave was observed up to 1.8V. For **3h**, however, only one

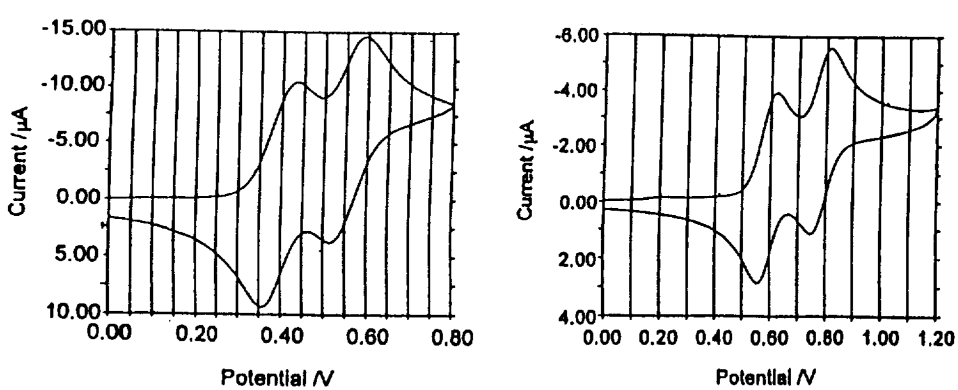


Fig .1 CV curves for **3f** (left) and **3g** (right) at 25℃

Table 3. The Redox Potentials $(E^{o'})^a$ for **3f** and **3g** in n-PrCN at 25℃^{b}.

3	**3f**		**3g**	
$E^{o'}$(mV)	395	556	591	782
ΔE_p(mV)	79	74	62	65

a Potentials vs Ag/Ag$^+$. $E^{o'}=(E_{ox}+E_{red})/2$.

b n-PrCN containing 0.1M n-Bu_4NPF_6 was used. The scan rate was 100mV/s.

irreversible oxidation wave was observed. These results indicate that the protecting substituent groups on both the central and outer phenyl rings play an important role in stabilizing mono- or dications of **3**.

An ESTN spectroscopy as a novel technique[4] was invoked in order to equivocally identify the spin multiplicity of the dicationic state of **3** (abbreviated to $\mathbf{3}^{2+}$), exemplifying $\mathbf{3f}^{2+}$ which was generated by chemical oxidation of **3f** in CH_2Cl_2 containing tetra-*n*-butylammonium tetrafluoroborate and lead tetraacetate. A small amount of trifluoroacetate anhydride was added to the CH_2Cl_2 solution to perform the complete oxidation.[21] The ESTN spectroscopy based on pulsed ESR techniques is a powerful tool to discriminate between spin multiplicities even in the mixtures of different spins. Figure 2 shows a conventional cw-ESR spectrum of $\mathbf{3f}^{2+}$ observed at 7K in a CH_2Cl_2 glass. The salient spectroscopic features of the triplet ground state expected for $\mathbf{3f}^{2+}$ are apparently vague and unreliable. Particularly, they are masked by the strong centered peak due to by-products. Figure 3 exemplifies a contour plot of field-swept 2D ESTN spectra of $\mathbf{3f}^{2+}$ under the same conditions as for the cw-ESR spectrum. At 23.1MHz two peaks dominate and at 15.3MHz a single peak does, as seen in Fig. 3.

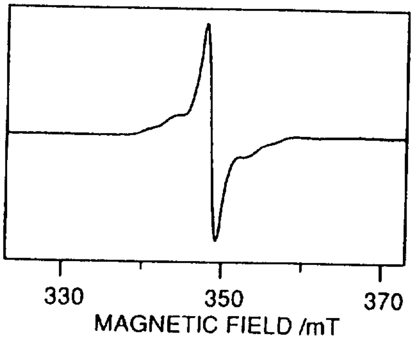


Fig. 2 Conventional cw-ESR spectrum of $\mathbf{3f}^{2+}$ observed at 7K in a CH_2Cl_2 glass.

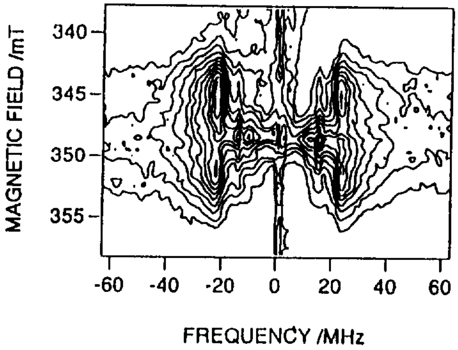


Fig. 3 Contour plot of field-swept 2D nutation spectra of $\mathbf{3f}^{2+}$ observed at 7K in a CH_2Cl_2 glass.

The nutation frequency ω_n (S=1) for |S=1, Ms=0>⇔|S=1, Ms= ±1> ESR transitions is given by $\sqrt{2}\ \omega_1$ (ω_1 proportional to the microwave field employed), while the nutation frequency ω_n (S=1/2) by ω_1. Thus, the observed ratio of 23.1/15.3 agrees with the theoretical value $\sqrt{2}\omega_1/\omega_1$ within experimental error, unequivocally illustrating that the cw-ESR spectrum is comprised of a triplet and doublet chemical species. The observed fine-structure constants (|D|=0.007cm^{-1}, E=0) for the triplet species with g=2.00 are in accordance with those of a tricationic quartet-state 1,3,5-tris(diarylamino)benzene if the projection factor of spin quantum numbers is taken into account, indicating that the observed fine structure is due to the triplet state of $\mathbf{3f}^{2+}$. The temperature dependence of the fine structure spectra indicated that the triplet state is a ground state or a nearby excited state within ~5cm^{-1}. An increase in torsional angles between the phenyl rings at the nitrogen atomic sites of **3** gives rise to the pronounced preference for a singlet ground state. In this context, the increase is a competitive factor against the high-spin preference due to the π-topological pseudo degeneracy and the dicationic **3a-e** are expected to favor triplet ground states although not yet isolated. Details of the ESTN spectroscopic results will be published elsewhere.

In conclusion, the triplet state of the dicationic state of 1,3-bis(diarylamino)benzene **3f** has been for the first time detected, indicating the potential capability of π-topological pseudo degeneracy in building extended polycationic high-spin systems.

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3. NMR measurements were performed in $CDCl_3$ using TMS as internal standard. ^{1}H-NMR was run at 400 MHz and ^{13}C-NMR at 100MHz. **3c**: ^{1}H-NMR δ 6.64 (dd, 2H, J=8.26, 1.84Hz), 6.95 (t, 1H, J=1.84 Hz), 7.04~7.22 (m, 17H). ^{13}C-NMR δ 118.39, 119.72, 122.67, 124.10, 129.11, 129.73, 147.55, 148.61. **3f**: ^{1}H-NMR δ 1.97 (s, 6H), 3.75 (s, 12H), 6.71 (d, 8H, J=9.16Hz), 6.82~6.84 (m, 9H), 7.02 (s, 1H). ^{13}C-NMR δ 18.20, 55.53, 114.37, 122.58, 129.21, 132.84, 132.87, 134.49, 141.49, 141.64, 154.17. **3g**: ^{1}H-NMR δ 1.98 (s, 6H), 2.25 (s, 12H), 6.82 (d, 8H, J=7.96Hz), 6.94 (s, 1H), 6.96 (d, 8H, J=7.96Hz), 7.06 (s, 1H). ^{13}C-NMR δ 18.15, 20.65, 121.14, 129.50, 130.32, 130.49, 134.05, 134.51, 144.48, 145.06. Identification data (IR, ^{1}H-, ^{13}C-NMR etc.) for all **3** were satisfsfactory for each desired structure. Data only for **3c**, **3f**, and **3g** are given above.
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