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Author(s)	Sakamaki, Daisuke; Ito, Akihiro; Furukawa, Ko; Kato, Tatsuhisa; Tanaka, Kazuyoshi
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High-spin polycationic states of an alternate *meta–para*–linked oligoarylamine incorporating two macrocycles†

Daisuke Sakamaki,[a] Akihiro Ito,*[a] Ko Furukawa,[b] Tatsuhisa Kato,[c] and Kazuyoshi Tanaka[a]

High-spin alignment for dicationic, tricationic, tetracationic, and hexacationic species of a *meta-para*-linked oligoarylamine was accomplished by incorporating cyclophane skeletons into the oligomer backbone.

Poly(radical cation) form of poly(*m*-aniline) (Fig. 1(a)), the position isomer of polyaniline as the well-known conductive polymer, is anticipated to be a candidate of the ferromagnetic polymers from the viewpoint of superdegeneracy among the half-filled bands,[1] and has been investigated so far through the direct polymerization study[2–4] and the oligomer model study.[5–7] Afterwards, it has been widely accepted that the semi-quinone radical cation of *para*-phenylenediamine (PD) moiety is far more stable than the aminium radical cation as the spin-containing unit in poly(*m*-aniline), and therefore, the main forcus has been shifted to the alternating *meta-para*-isomers of polyaniline and/or oligoaniline.[8–10] Recently, Kulszewicz-Bajer and co-workers have conducted elaborative work on the oxidized form of poly(*m*-*p*-aniline) (Fig. 1(b)), and as a consequence, the generated spins in the polymer were shown to be mainly uncoupled ($S = 1/2$) except for the existence of minor triplet ($S = 1$) spin clusters.[10] Furthermore, their unfortunate results are also supported from our oligomer model study.[11]
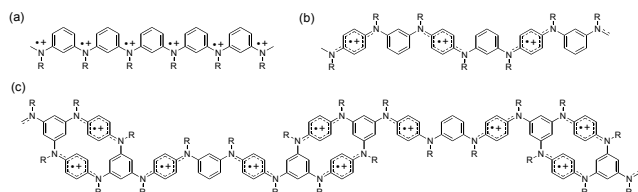

Fig. 1 Poly(radical cation)s of (a) poly(*m*-aniline), (b) poly(*m*-*p*-aniline), and (c) cyclophane-containing poly(*m*-*p*-aniline).

On the other hand, we have demonstrated that the high-spin alignment has been fulfilled for the macrocyclic oligomers of poly(*m*-aniline) and/or poly(*m*-*p*-aniline), and hence, the macrocyclic oligoanilines can be effectively utilized as the promising high-spin building blocks to construct the two- and three-dimensional multi-spin system.[12] In particular, tetraaza[1_4]*m*,*p*,*m*,*p*-cyclophane has a definite molecular structure, and moreover, can be feasibly derived to pure spin triplet species by two-electron-oxidation.[12a,13] In this context, the introduction of the cyclophane moieties into the polymer backbone may bring in good results to obviate the uncoupled

spin difficulty in the one-dimensional poly(*m*-*p*-aniline). As a first step to verify the validity of the cyclophane-containing poly(*m*-*p*-aniline) (Fig. 1(c)), we prepared a *meta-para*-linked oligoarylamine **1** incorporating two cyclophane moieties, which is comprised of a central linearly-linked moiety and two peripheral cyclophane moieties.
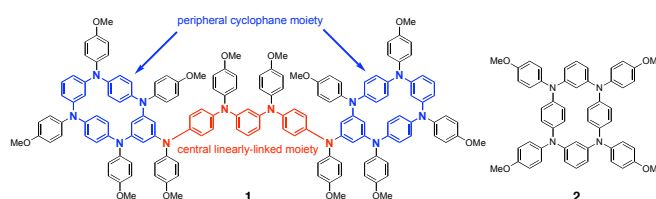
As shown in Fig. 2, the frontier molecular orbitals (MO) are predicted to be virtually six-fold quasi-degenerate non-disjoint π-MOs,[14] judging from the simple Hückel MO calculation of a model compound.
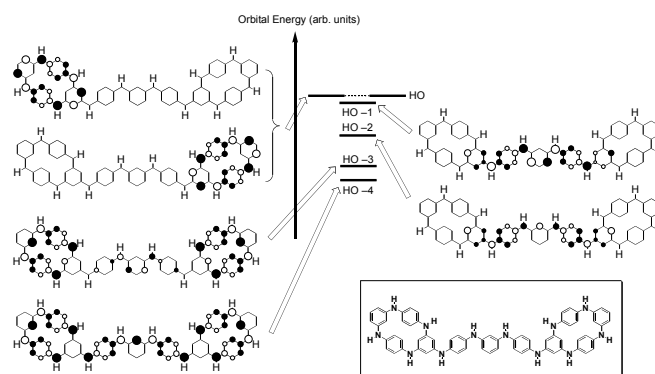

Fig. 2 Schematic drawing of the frontier MOs for a model compound of **1**.

The target molecule **1** has been prepared from *N,N',N''*-tris(4-anisyl)-1,3,5-benzenetriamine (**3**)[15] and *N,N'*-di(4-bromophenyl)-*N,N'*-di(4-anisyl)-1,3-benzenediamine (**4**)[13b] using a 2:3 ratio of substrates by performing the palladium-catalyzed aryl amination reaction (Buchwald-Hartwig reaction)[16] in a one-pot manner (Scheme 1, ESI†).
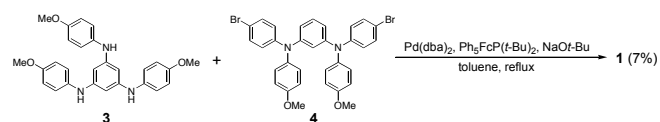
Scheme 1 Synthesis of *meta-para*-linked oligoarylamine incorporating two tetraazacyclophane **1**.

As shown in Fig. S1(ESI†), the cyclic voltammogarm of **1** in CH_2Cl_2 showed six redox couples at –0.04, +0.08, +0.16, +0.26, +0.59, and +0.68 V (*vs.* Fc/Fc$^+$), which tentatively

correspond to oxidation processes, 1^0 to 1^{2+}, 1^{2+} to 1^{3+}, 1^{3+} to 1^{4+}, 1^{4+} to 1^{6+}, 1^{6+} to 1^{10+}, and 1^{10+} to 1^{12+}, respectively, judging from the differential pulse voltammogram (Fig. S2, ESI†). This indicates that 1 is oxidizable up to dodecacation: as compared to the first and second oxidation potentials (−0.01 and +0.02 V) and the third and forth oxidation potentials (+0.54 and 0.67 V) of tetraazacyclophane 2,[12c] the first 4 redox couples correspond to the generation of 6 semi-quinoidal PD radical cations, while the remaining 2 redox couples to the generation of 6 quinoidal PD dications to produce diamagnetic (*i.e.* spinless) species; in the first oxidation process, two electrons are removed simultaneously from the two peripheral tetraazacyclophane moieties, so as to reduce the electrostatic repulsions between the charged semi-quinoidal PD units; the subsequent two one-electron-oxidation processes take place from the central two PD units; finally, two electrons are removed furthermore simultaneously from the two peripheral tetraazacyclophane moieties to generate the hexa(radical cation) of 1. This conjecture is in good accordance with the Hückel MO pictures having the six-fold quasi-degenerate frontier MOs including the doubly degenerate HOMOs (Fig. 2).

The UV-Vis-NIR spectral change during the course of the electrochemical oxidation of 1 was monitored by using an optically-transparent thin-layer electrochemical cell (Fig. 3). As the oxidation proceeds, three new bands appeared at 426, 605, and ~1100 nm. The broad band (~1100 nm) in the NIR region is considered to be the intervalence band between the aminium radical cation center and the neutral amine center, and is composed of two bands at ~1000 and ~1200 nm. On going from 1^{2+} to 1^{6+}, it was found that the intensity of the higher energy band (~1000 nm) was gradually strengthened as compared to that of the lower energy band (~1200 nm), suggesting the charge-localization in the higher oxidation states of 1. When 1^{6+} is further oxidized, a new intense band at 810 nm grew with an isosbestic point at 892 nm, corresponding to the conversion of the semi-quinoidal PD radical cation moieties to the diamagnetic quinoidal PD dication ones.
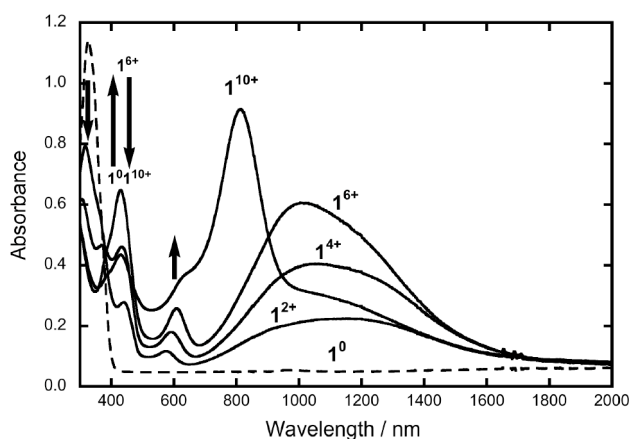

Fig. 3 UV–Vis–NIR spectra of the stepwise electrochemical oxidation of 1 to decacation 1^{10+} in CH_2Cl_2/0.1 M n-Bu$_4$NBF$_4$ at 298 K.

Encouraged by the observed electrochemical multi-stage oxidation processes, we have measured the continuous wave ESR (cw-ESR) spectra of 1^+, 1^{2+}, 1^{3+}, 1^{4+}, and 1^{6+} in a rigid-glass of CH_2Cl_2 at 123K.[17] Each oxidized species were generated by adding 1 to 6 molar equivalents of tris(4-bromophenyl)aminium hexachroloantimonate[18] at 195 K. As is often the case with the high-spin molecules possessing delocalized spin centers, however, neither the definitive fine-structure in the allowed resonance ($\Delta M_S = \pm 1$) nor the forbidden resonance ($\Delta M_S = \pm 2$) were detected (Fig. S3, ESI†).[19] These results prompted us to measure the electron spin transient nutation (ESTN) measurements based on the pulsed ESR method (ESI†).[20]

As shown in Fig. 4, the observed 2-dimensional ESTN (2D-ESTN) spectra clearly displayed the change of spin-multiplicity corresponding to the stepwise-oxidized species of 1. The nutation frequency components observed at 5 K for each oxidation state of 1 are summarized in Table 1. Besides the unknown doublet impurity, the triplet and quartet signals were seen in 1^{2+} and 1^{3+}, strongly indicating the high-spin alignment among the semi-quinoidal PD radical cations generated from the peripheral cyclophane moieties and the central linearly-linked moiety. In the higher oxidation states, 1^{4+} and 1^{6+}, the competing intermediate spin states (*i.e.* triplet and/or quintet states) were also detected in addition to the predicted quintet and septet states, suggesting that the high-spin state is nearly degenerate with thermally accessible intermediate spin states. As a consequence of introduction of macrocycles, the hope of the high-spin organic polymers can be pinned on the *meta-para*-linked polyarylamines.

Table 1 Spectral data of the 2D-ESTN spectroscopy for poly(radical cation)s of 1

Species	Obsd. nutation frequency (in MHz)	Transition assignment
1^{2+}	24.8 ($\cong \sqrt{2}\,\omega_{doublet}$)	$\|1, \pm 1\rangle \Leftrightarrow \|1, 0\rangle$
(doublet impurity	18.0 ($= \omega_{doublet}$)	$\|1/2, +1/2\rangle \Leftrightarrow \|3/2, -1/2\rangle$)
1^{3+}	34.3 ($\cong \sqrt{3}\,\omega_{doublet}$)	$\|3/2, \pm 3/2\rangle \Leftrightarrow \|3/2, \pm 1/2\rangle$
	39.0 ($\cong 2\,\omega_{doublet}$)	$\|3/2, +1/2\rangle \Leftrightarrow \|3/2, -1/2\rangle$
(doublet impurity	20.0 ($= \omega_{doublet}$)	$\|1/2, +1/2\rangle \Leftrightarrow \|3/2, -1/2\rangle$)
1^{4+}	36.4 ($\cong \sqrt{2}\,\omega_{triplet}$)	$\|2, \pm 2\rangle \Leftrightarrow \|2, \pm 1\rangle$
	44.5 ($\cong \sqrt{3}\,\omega_{triplet}$)	$\|2, \pm 1\rangle \Leftrightarrow \|2, 0\rangle$
(competing triplet	26.0 ($= \omega_{triplet}$)	$\|1, \pm 1\rangle \Leftrightarrow \|1, 0\rangle$)
1^{6+}	44.4 ($\cong \sqrt{3}\,\omega_{triplet}$)	$\|2, \pm 2\rangle \Leftrightarrow \|2, \pm 1\rangle$
	56.8 ($\cong \sqrt{5}\,\omega_{triplet}$)	$\|2, \pm 1\rangle \Leftrightarrow \|2, 0\rangle$
	62.9 ($\cong \sqrt{6}\,\omega_{triplet}$)	$\|2, \pm 1\rangle \Leftrightarrow \|2, 0\rangle$
(competing quintet	34.0 ($= \sqrt{2}\,\omega_{triplet}$)	$\|2, \pm 2\rangle \Leftrightarrow \|2, \pm 1\rangle$
	44.0 ($= \sqrt{3}\,\omega_{triplet}$)	$\|2, \pm 1\rangle \Leftrightarrow \|2, 0\rangle$)
(competing triplet	25.0 ($= \omega_{triplet}$)	$\|1, \pm 1\rangle \Leftrightarrow \|1, 0\rangle$)

80

(a)

ω_triplet

ω_doublet

Magnetic Field / mT

Nutation Frequency / MHz

(b)

ω_quartet,1

ω_doublet   ω_quartet,2

Magnetic Field / mT

Nutation Frequency / MHz

(c)

ω_quintet,1

ω_triplet   ω_quintet,2

Magnetic Field / mT

Nutation Frequency / MHz

(d)

ω_triplet   ω_quintet,1   ω_septet,1 ω_septet,2

ω_quintet,2   ω_septet,3

Magnetic Field / mT

Nutation Frequency / MHz

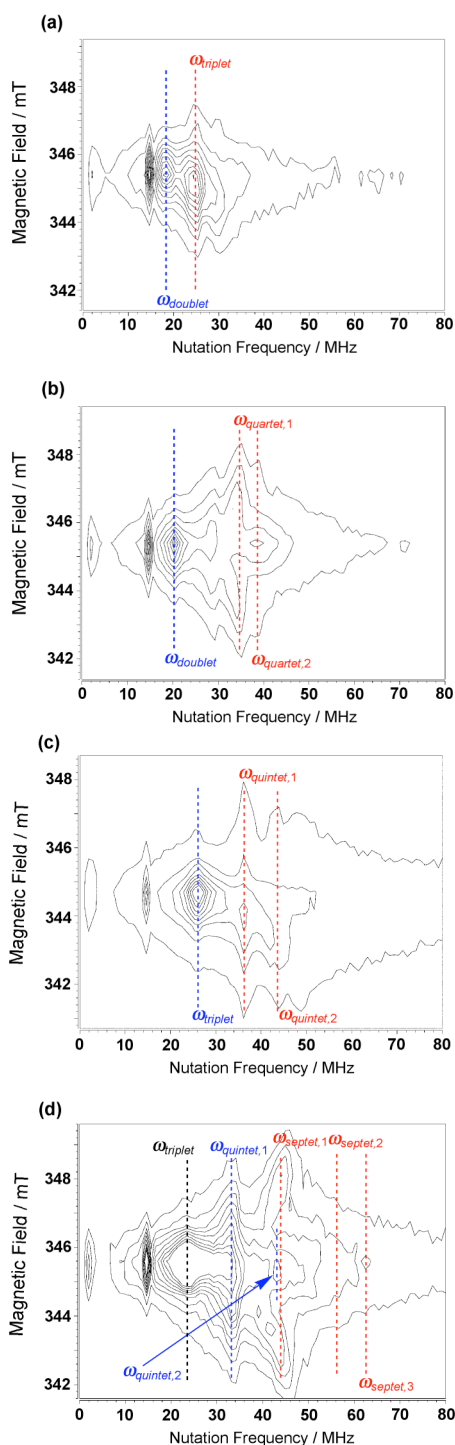**Fig. 4** 2D-ESTN spectra of **1** in CH_2Cl_2 at 5K after the addition of (a) 2 equiv., (b) 3 equiv., (c) 4 equiv., and (d) 6 equiv. of oxidant.

Notes and references

[a] Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan. E-mail: aito@scl.kyoto-u.ac.jp
[b] Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan
[c] Department of Chemistry, Josai University, 1-1 Keyakidai, Sakado, Saitama 350-0295, Japan

† Electronic Supplementary Information (ESI) available: Experimental section and the electrochemical and ESR spectroscopic data. See DOI: 10.1039/b000000x/

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17 The present poly(radical cation)s were found to be far more stable than the oxidized oligo(*m*-aniline)s, which immediately decompose at room temperature or lower temperatures. For instance, about 80 % of the hexacation of **1** survive in solution after 1 hr at room temperature, judging from the ESR intensity.

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