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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,b Ko Furukawa,a Tatsuhisa Kato,c and Kazuyoshi Tanakaa

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Poly(radical cation) form of poly(m-aniline) (Fig. 1(a)), the high-spin 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, and has been investigated so far through the direct polymerization study and the oligomer model study. Afterwards, it has been widely accepted that the semi-quinone radical cation of para-phenylenediamine (PD) moiety is far more stable than the aminon radical cation as the spin-containing unit in poly(m-aniline), and therefore, the main focus has been shifted to the alternating meta–para-isomers of polyaniline and/or oligoaniline. Recently, Kulszewicz-Bajer and co-workers have conducted elaborate 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. Furthermore, their unfortunate results are also supported from our oligomer model study.

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 oligoamines can be effectively utilized as the promising high-spin building blocks to construct the two- and three-dimensional multi-spin system. In particular, tetraaza[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. 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, judging from the simple Hückel MO calculation of a model compound. The target molecule 1 has been prepared from N,N',N'-tris(4-anisyl)-1,3,5-benzenetramine (3) and N,N'-di(4-bromophenyl)-N,N'-di(4-anisyl)-1,3-benzenetramine (4) using a 2:3 ratio of substrates by performing the palladium-catalyzed aryl amination reaction (Buchwald-Hartwig reaction) in a one-pot manner (Scheme 1, ESIF).

As shown in Fig. S1(ESIF), the cyclic voltammogram of 1 in CH2Cl2 showed six redox couples at −0.04, +0.08, +0.16, +0.26, +0.59, and +0.68 V (vs. Fe/Fe3+), which tentatively

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

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

Scheme 1 Synthesis of meta–para–linked oligoarylamine incorporating two tetraazacyclophane 1.

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ESR (cw-ESR) spectra of 1+, 12+, 13+, 14+, and 16+ in a rigid
glass of CH2Cl2 at 123 K. Each oxidized species were
generated by adding 1 to 6 molar equivalents of tri(4-
 bromophenyl)ammonium hexachloroantimonate at 195 K. As is
typical with the high-spin molecules possessing
delocalized spin centers, however, neither the definitive fine-
structure in the allowed resonance (ΔM5 = ±1) nor the
forbidden resonance (ΔM5 = ±2) were detected (Fig. S3, ESI†).
These results prompted us to measure the electron
spin transient nutation (ESTN) measurements based on the
pulsed ESR method (ESI†).
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 10+ and 11+, 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,
10+ and 11+, 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.

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Scientific Research (B) (20350065) from Japan Society for
the Promotion of Science (JSPS). Thanks are due to the Research
Center for Molecular-Scale Nanoscience, the Institute for
Molecular Science for use of the pulsed ESR spectrometer.

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

<table>
<thead>
<tr>
<th>Species</th>
<th>Obsd. nutation frequency (in MHz)</th>
<th>Transition assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>10+</td>
<td>24.8 (± 2ω_{spin})</td>
<td>1, ±1 ⇔</td>
</tr>
<tr>
<td>(doublet impurity)</td>
<td>18.0 (±ω_{spin})</td>
<td>1/2, ±1/2 ⇔ 3/2, −1/2&gt;</td>
</tr>
<tr>
<td>11+</td>
<td>34.3 (± 3ω_{spin})</td>
<td>3/2, ±3/2 ⇔ 3/2, ±1/2&gt;</td>
</tr>
<tr>
<td></td>
<td>39.0 (± 2ω_{spin})</td>
<td>3/2, ±1/2 ⇔ 3/2, −1/2&gt;</td>
</tr>
<tr>
<td>(doublet impurity)</td>
<td>20.0 (±ω_{spin})</td>
<td>1/2, ±1/2 ⇔ 3/2, −1/2&gt;</td>
</tr>
<tr>
<td>12+</td>
<td>36.4 (± 2ω_{spin})</td>
<td>2, ±2 coin 1, ±1&gt;</td>
</tr>
<tr>
<td></td>
<td>44.5 (± 3ω_{spin})</td>
<td>2, ±1 ⇔ 2, 0&gt;</td>
</tr>
<tr>
<td>(competing triplet)</td>
<td>26.0 (±ω_{spin})</td>
<td>1, ±1 ⇔ 1, 0&gt;</td>
</tr>
<tr>
<td>13+</td>
<td>44.4 (± 3ω_{spin})</td>
<td>2, ±2 ⇔ 2, ±1&gt;</td>
</tr>
<tr>
<td></td>
<td>56.8 (± 5ω_{spin})</td>
<td>2, ±1 ⇔ 2, 0&gt;</td>
</tr>
<tr>
<td></td>
<td>62.9 (± 6ω_{spin})</td>
<td>2, ±1 ⇔ 2, 0&gt;</td>
</tr>
<tr>
<td>(competing quintet)</td>
<td>34.0 (± 2ω_{spin})</td>
<td>2, ±2 ⇔ 2, ±1&gt;</td>
</tr>
<tr>
<td>14+</td>
<td>44.0 (± 5ω_{spin})</td>
<td>2, ±1 ⇔ 2, 0&gt;</td>
</tr>
<tr>
<td></td>
<td>25.0 (±ω_{spin})</td>
<td>1, ±1 ⇔ 1, 0&gt;</td>
</tr>
</tbody>
</table>

Encouraged by the observed electrochemical multi-stage
oxidation processes, we have measured the continuous wave

![Graph](image-url)
Notes and references


13. The present poly(radical cation)ns were found to be far more stable than the oxidized oligo(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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