A novel trimacroyclic arylamine was found to be accessible to the different spin-states by consecutive electrochemical or chemical oxidation.

Alternating meta-phenylene- and para-phenylene-linked oligoarylamines are considered as promising molecular parts for the molecule-based electronics due to their intriguing magnetic and electronic properties. From the magnetic point of view, meta-phenylene linker plays a role in ensuring the effective ferromagnetic interaction, while para-phenylene linker takes an important part in stabilizing the spin-containing amine radical cations. Of the meta-para oligoarylamines prepared so far, the macrocyclic oligoarylamines are structurally defined and, therefore, we can employ them as the component pieces to prepare the two- and/or three-dimensionally structured oligoarylamines. The synthesis of tetraaza[1,4]m,p,m,p-cyclophanes, the smallest macrocyclic oligoarylamines possessing the alternating meta-para linkage, has been reported independently at the same time by three groups (Fig. 1(a)). Expectedly, these molecules were oxidized into di(radical cation) with parallel spin-orientation. Moreover, recently, Hartwig and co-workers have succeeded in synthesizing three- and four-runged ladder-type oligoarylamines (Fig. 1(b)). However, the ground state of the dications was determined to be a spin-singlet, although the generated spins are of delocalized character.

When the tetraazacyclopheane structure in Fig. 1(a) is utilized as a building block for constructing the trimacroyclic oligoarylamine molecular system such as the ladder-type molecule in Fig. 1(b), there exists another option; the star-shaped extension. For the purpose of elucidating the electronic structures of polycationic species of the star-shaped trimacro cyclic oligoarylamine, we synthesized a macrocycle 1 in around 10% yield, in a one-pot reaction (Scheme 1).

Electrochemical oxidation of the trimacrocycle 1 by the cyclic voltammetry (CV) in CH₂Cl₂ exhibits five redox couples as shown in Fig. 2. All the oxidation processes are chemically reversible after repeated potential cycling in CH₂Cl₂. Judging from the differential pulse voltammogram (Fig. S1, ESI†), the first four oxidations are regarded as one-electron transfer process, while the fifth oxidation corresponds to quasi-two-electron transfer, indicating 1 is oxidizable up to hexacation. The oxidation potentials of 1 are summarized in Table 1 together with those of the related compounds under the same conditions.
From the comparison of the oxidation potentials for 1 with those for the star-shaped analog 2, the first three oxidations are assigned as one-electron removal from each peripheral triamine moiety. Each oxidation potential of 1 shifts to the higher value as compared with the corresponding value of 2. This situation closely relates to the fact that all the nitrogen atoms are inevitably charged after the three-electron removal from 1, and therefore, the electrostatic repulsion on the peripheral meta-phenylenediamine moieties cannot be ignored, as shown in Fig. 3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_1$</th>
<th>$E_2$</th>
<th>$E_3$</th>
<th>$E_4$</th>
<th>$E_5$</th>
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<tr>
<td>1</td>
<td>-0.12</td>
<td>0.09</td>
<td>0.28</td>
<td>0.41</td>
<td>0.53$^b$</td>
</tr>
<tr>
<td>2</td>
<td>-0.14</td>
<td>-0.01</td>
<td>0.09</td>
<td>0.19$^d$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-0.11</td>
<td>0.25</td>
<td>0.80$^c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>-0.01</td>
<td>0.22</td>
<td>0.54</td>
<td>0.67</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ 1 mM CH$_2$Cl$_2$ solution containing 0.1 M n-Bu$_4$NBF$_4$; potentials versus Fe/Fc$,^c$, Pt electrode, 298 K, scan rate 100 mV s$^{-1}$. $^b$Quasi-two-electron transfer. $^c$Measured in PhCN (see ref. 3(c)). $^d$Quasi-three-electron transfer. $^e$Anodic peak potential (irreversible).

We measured the optical absorption spectral changes of 1 in CH$_2$Cl$_2$ during the oxidation process of 1 to 1$^{3+}$ by using an optically transparent thin-layer electrochemical cell. As shown in Fig. 4, the lowest-energy absorption band at $\lambda_{\text{max}} = 1154$ nm emerged together with the shoulder band at $\sim 900$ nm upon oxidation of 1 to 1$^+$. Further oxidation to the dication 1$^{2+}$ resulted in blue shift and increase in intensity of the lowest-energy band ($\lambda_{\text{max}} = 1051$ nm). Finally, in the resulting trication 1$^{3+}$, further blue shift and increase in intensity of the lowest energy band ($\lambda_{\text{max}} = 1051$ nm) were observed. Note that the similar spectral change was also seen during the oxidation process of 5 to 5$^{2+}$ (Fig. S2). The spectral change in the charged states of 5 is expected to be influenced by the charge difference between 5$^+$ and 5$^{2+}$; the generated charge in 5$^+$ is considered to be distributed over the central triphenylenediamine moiety, whereas that in 5$^{2+}$ is localized mainly on the outer two triphenylenediamine moieties to avoid the electrostatic repulsion. Therefore, it is anticipated that the charge distribution in the charged states of 1 changes from the central 1,3,5-triaminobenzene moiety to the peripheral three meta-phenylenediamine moieties, on going from 1$^+$ to 1$^{3+}$ (Fig. 3). This speculation can be supported by the comparison of the oxidation potentials for 1 with those for the triamine moiety 5 (Table 1). The first oxidation potentials of both 1 and 5 show almost the same value, while the third oxidation potential of 1 is similar to the second oxidation potential of 5.

To explore the spin state of the each oxidized state of 1, we measured the continuous wave ESR (cw-ESR) spectra of 1$^+$, 1$^{2+}$, 1$^{3+}$ and 1$^{4+}$ in the rigid-glass.$^7$ However, neither the definitive fine-structured spectra$^6$ nor the forbidden resonance$^6$ due to the existence of high-spin species were observed at 123 K (Fig. S3, ESI†). To overcome the difficulty in identifying the spin multiplicity of the high-spin components, we carried out the electron spin transient nutation (ESTN) measurements$^8$ based on the pulsed ESR method (Figs. 5 and S4, ESI†). As shown in Fig. S4a (ESI†), the nutation frequency (18 MHz = $\omega_{\text{citation}}$ = $\omega_{\text{doublet}}$) observed at the central field is ascribed to $|1/2, -1/2\rangle \leftrightarrow |1/2, +1/2\rangle$ transition of the spin-doublet 1$^+$. For the sample treated by 2 molar equiv of oxidant, the new $\gamma$ signal with the nutation frequency of 22 MHz (= $\omega_{\text{citation}}$) appeared, and this corresponds to the $|1, 0\rangle \leftrightarrow |1, \pm 1\rangle$ transition for spin-triplet state (Fig. 5a). The generated triplet species can be regarded as 1$^{3+}$. After oxidation of 1 with 3 molar equiv of oxidant, two new intense signals with the same $\gamma$ nutation frequency of 33 MHz (= $\omega_{\text{trication}}$) were seen in
addition to that for the spin-triplet species ($\omega_{\text{triplet}} = 24 \text{ MHz}$) as impurities in the sample (Fig. 5b). From the frequency ratio ($\omega_{\text{triplet}} / \omega_{\text{doublet}} \sim \sqrt{3}$), these nutation signals are assigned to the $\pm 3/2, \pm 1/2$ transition for spin-quartet state, clearly indicating the dominance of spin-quartet $1^4\text{+}$. Finally, when 4 molar equiv of oxidant is added, the observed nutation signals were detected at 25 MHz, corresponding to the generation of spin-triplet species on the basis of the frequency ratio ($\omega_{\text{triplet}} / \omega_{\text{doublet}} \sim \sqrt{2}$) (Fig. S4b, ES I†). Considering the quantity of added oxidant, the observed triplet species is considered as $1^3\text{+}$. This results suggests the newly generated spin is antiferromagnetically coupled to the existing three spins. As a whole, the consecutive oxidations of $1$ lead to the charged states $1^1\text{+}$, $1^2\text{+}$, $1^3\text{+}$, and $1^4\text{+}$ with doublet, triplet, quartet, and triplet spin multiplicities, respectively, at low temperature.

In summary, we have prepared a novel trimacrocyclic arylamine with a rigid molecular structure. From the electrochemical study, it was confirmed that this trimacrocycle is oxidizable up to the hexacation, and the chemically generated dication and trication are in high-spin state. Trimacrocycle $1$ is not easily dissolve in polar solvents such as CH$_2$Cl$_2$, n-butylonitrile, and so forth, and thus, the measurements were executed only by using a dilute solution of toluene/n-butylonitrile. Therefore, we could not observe the forbidden $\Delta M_S = \pm 1$ resonance.

The present work was supported by Grant-in-Aid for Scientific Research (B) (20350065) from the Japan Society for the Promotion of Science (JSPS) and from CREST (Core Research for Evolutional Science and Technology) of the Japan Science and Technology Agency (JST). Thanks are due to the Research Center for Molecular –Scale Nanoscience in the Institute for Molecular Science for the use of a pulsed ESR spectrometer.

Notes and references

24. The stepwise chemical oxidation with tris(4-bromophenyl)ammonium hexachloroantimonate (TBA+SbCl$_5$) at 195 K in toluene/n-butylonitrile (8:2 (v/v)) generated the corresponding radical cations $1^1\text{+}$ to $1^4\text{+}$. Trimacrocycle $1$ does not easily dissolve in polar solvents such as CH$_2$Cl$_2$, n-butylonitrile, and so forth, and thus, the measurements were executed only by using a dilute solution of toluene/n-butylonitrile. Therefore, we could not observe the forbidden $\Delta M_S = \pm 1$ resonance.

Fig. 5 2D ESTN spectra of $1$ in toluene/n-hexane at 5 K after the addition of (a) 2 equiv and (b) 3 equiv of oxidant.
Supplementary Information for:

Trimacrocyclic Arylamine and its Polycationic States

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\[ \text{N, N', N''-tris(4-chlorophenyl)-1,3,5-benzenetriamine (3).} \]

To a mixture of phloroglucinol (1.26 g, 10.0 mmol), 4-chloroaniline (5.75 g, 45.1 mmol), and iodine (0.156 g, 0.6 mmol) was added toluene (5 ml) under argon atmosphere, and then the reaction mixture was refluxed with stirring for 29 h. After evaporation of the solvent, the residue was thoroughly washed with MeOH to afford 3 (3.87 g, 85%) as a purple solid: mp 232–234 °C; \(^1\)H NMR (400 MHz, tetrahydrofuran-\(d_8\)) \(\delta\) 7.29 (s, 3H), 7.14 (d, \(J = 8.8 \) Hz, 6H), 7.02 (d, \(J = 8.8 \) Hz, 6H), 6.32 (s, 3H); \(^13\)C NMR (100 MHz, tetrahydrofuran-\(d_8\)) \(\delta\) 145.83, 143.60, 129.46, 124.76, 119.40, 100.05; EI HRMS (\(m\)-nitrobenzyl alcohol) \(m/z\) (relative intensity %) calcd for C\(_{24}\)H\(_{18}\)N\(_3\)O\(_3\) [M]\(^+\) 453.0566, found 453.0569 (100).
\(N,N',N'',N'''-hexa\text{is}(4\text{-chlorophenyl})-1,3,5\text{-benzenetriamine (4).}\) \(p\text{-Bromochlorobenzene (8.63 g, 45.0 mmol)}, 3 (1.37 g, 3.00 mmol), NaOrBu (1.29 g, 13.5 mmol), Pd(OAc)\text{)}_2 (34 mg, 0.15 mmol), and 1,1'\text{-bis(diphenylphosphanyl)ferrocene (DPPF) (0.174 g, 0.30 mmol)}\) were dissolved in toluene (30 ml) under argon atmosphere. The resulting solution was refluxed for 32 h with stirring. After evacuation of the solvent, CH\text{2Cl2} and saturated aqueous solution of NaCl were added to the residue. The resulting organic layer was dried over MgSO\text{4}, filtered, and concentrated. The residue was purified on column chromatography on silica gel using ethyl acetate / \(n\text{-hexane (1:1 (v/v))},\) and was further recrystallized from ethyl acetate / \(n\text{-hexane to yield 4 (1.89 g, 80\%)}\) as a white solid: mp 206–208 °C; \(^1\text{H NMR (400 MHz, C}_6\text{D}_6) \delta 6.90 (d, J = 8.8 Hz, 12H), 6.65 (d, J = 8.8 Hz, 12H), 6.96 (s, 2H), 6.86 (t, J = 6.0 Hz, 2H), 6.84 (d, J = 9.2 Hz, 16H), 6.78 (s, 2H), 6.78 (d, J = 8.7 Hz, 8H), 6.43 (s, 3H); \(^{13}\text{C NMR (100 MHz, C}_6\text{D}_6) \delta 149.3, 145.3, 130.0, 129.1, 125.6, 113.0;\) EI HRMS (\(m\text{-nitrobenzyl alcohol}) m/z\) (relative intensity %) calcd for C\text{42H27N3O6 [M]}^+ 783.0336, found 783.0336 (49.9).
Trimacro cyclic arylamine (1). Anhydrous toluene (8 ml) was added into a mixture of 4 (314 mg, 0.40 mmol), N,N'-bis(4-methoxyphenyl)-1,3-benzenediamine [1] (772 mg, 2.41 mmol), Pd(dbach)\textsubscript{2} (13.7 mg, 0.024 mmol), Ph\textsubscript{5}FcP(t-Bu)\textsubscript{2} [2] (29.4 mg, 0.041 mmol), and sodium tert-butoxide (1.07 g, 11.3 mmol) in a flask under argon, and the solution was heated to reflux for 16 h. After filtration through Celite, the filtrate was chromatographed on a silica gel (toluene/ethyl acetate = 2:1 as eluent), and recrystallization from toluene/\textit{n}-hexane afforded 1 (58 mg, 9.5 %) as white powder: mp $> 300 \ ^\circ \text{C}$; \textsuperscript{1}H NMR (400 MHz, tetrahydrofuran-$d_8$) $\delta$ 7.06 (d, $J = 8.8$ Hz, 12H), 7.03 (d, $J = 8.8$ Hz, 12H), 6.88 (m(=t+d), 3H+12H), 6.81 (d, $J = 8.8$ Hz, 12H), 6.38 (dd, $J = 8.4$, 2.0 Hz, 6H), 6.33 (d, $J = 2.0$ Hz, 3H), 5.62 (s, 3H), 3.73 (s, 18H); \textsuperscript{13}C NMR (100 MHz, tetrahydrofuran-$d_8$) $\delta$ 157.19, 150.46, 150.29, 144.74, 142.66, 140.83, 133.98, 129.76, 128.14, 127.64, 126.40, 115.24, 113.97, 102.14, 55.50; FAB HRMS ($m$-nitrobenzyl alcohol) \textit{m/z} (relative intensity %) calcd for C\textsubscript{102}H\textsubscript{81}N\textsubscript{9}O\textsubscript{6} [M]$^+$ 1527.6310, found 1527.6316 (46.7).
Pulsed ESR Measurements: The magnetic moments with distinct spin quantum numbers ($S$) precess with their specific nutation frequency ($\omega_n$) in the presence of a microwave irradiation field and a static magnetic field. The nutation frequency for a transition from $|S, M_S >$ to $|S, M_S +1 >$ can be expressed as $\omega_n = [S(S+1) - M_S(M_S+1)]^{1/2} \omega_0$ under certain conditions. This indicates that $\omega_n$ can be scaled with the total spin quantum number $S$ and the spin magnetic quantum number $M_S$ in the unit of $\omega_n (= \omega_0)$ for the doublet species; $\sqrt{2}$ for $S = 1$, $\sqrt{3}$ and $2$ for $S = 3/2$. For determination of spin-multiplicity for high-spin molecules by using the pulsed ESR technique, see: (a) J. Isoya, H. Kanda, J. R. Norris, J. Tang and M. K. Brown, *Phys. Rev. B*, 1990, 41, 3905; (b) A. V. Astashkin and A. Schweiger, *Chem. Phys. Lett.*, 1990, 174, 595; (c) K. Sato, M. Yano, M. Furuichi, D. Shiomi, T. Takui, K. Abe, K. Itoh, A. Higuchi, K. Katsuma, Y. Shirota, *J. Am. Chem. Soc.*, 1997, 119, 6607. (d) H. Bock, K. Gharagozloo-Hubmann, M. Sievert, T. Prisner and Z. Havlas, *Nature*, 2000, 404, 267. (e) A. Ito, H. Ino, K. Tanaka, K. Kanemoto and T. Kato, *J. Org. Chem.*, 2002, 67, 491.

Pulsed ESR measurements were carried out on a Bruker ELEXES E580 X-band FT ESR spectrometer. The ESTN measurements were performed by the three-pulse sequence shown below. The two-pulse ($\pi/2 - \pi$ pulses) electron spin-echo signal $S(t_1)$ was detected by increasing the width
(t_1) of the nutation pulse. The observed signal S(t_1, B_0) as a function of external magnetic field B_0 is converted into a nutation frequency S(\omega_n, B_0) spectrum. The parameters used for the measurements were t_2 = 400 ns, t_3 = 8 ns.
Fig. S1. Differential pulse voltammogram of 1 measured in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NBF$_4$ at 298 K (scan rate 0.1 V s$^{-1}$).

\[ E / V \text{ vs } Fc/Fc^+ \]
Fig. S2. Vis-NIR spectra during the stepwise electrochemical oxidation of 5 in CH$_2$Cl$_2$/0.1M $n$-Bu$_4$NBF$_4$ at room temperature: 5$^+$ (dotted line) and 5$^{2+}$ (solid line).
Fig. S3. CW-ESR spectra of 1 at 123 K after addition of (a) 1 equiv, (b) 2 equiv, and (c) 3 equiv of oxidant.
Fig. S4. 2D ESTN spectra of 1 in toluene/\textit{n}-hexane (8:2 (v/v)) at 5 K after the addition of (a) 1 equiv and (b) 4 equiv of oxidant.