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A fully dianisylaminophenylated aza[14]metacyclophane is synthesized, which exhibits four reversible two-electron oxidation processes, and its dicationic and tetracationic species are found to be in spin-triplet and spin-quintet states.

There has been intensified interest in the heteroatom-bridged [14]metacyclophanes, in which conventional methylene bridges are replaced by heteroatoms, because of the unique properties attributable to the introduction of heteroatoms as bridging units.1 Such a new generation of macrocyclic compounds are of great importance in host-guest chemistry where highly selective molecular recognition is required for macrocyclic host compounds. From the different viewpoint, we focused on the nitrogen-bridged [14]metacyclophanes (or aza[14]metacyclophanes), and reported the preparation and properties of a series of aza[14]metacyclophanes.2 When nitrogen atoms are incorporated as bridging units into the aromatic compounds, they afford the multi-redox activity to the integrated molecular systems. In particular, polycyclic amines, in which meta-phenylenes are connected by nitrogen-bridging units, can be expected to become high-spin materials possessing the generated ammic radical cations as spin-bearing units after exhaustive oxidation procedure (Fig. 1(a)).3 In fact, poly(radical cation)s of several oligoarylamines are found to be in high-spin states.4 In this context, the oxidized species of the aza[14]metacyclophanes can be regarded as intriguing candidates for the toroidal molecular spin systems. In the polycyclicmethyl-based polyradicals, calix[4]arene-based macrocyclic high-spin molecules has already been reported.5

![Fig. 1 Poly(radical cation)s of (a) polycyclic amine and (b) aza[14]metacyclophane.](Image)

However, as has been exemplified by our previous studies,2 it proved impossible to realize the high-spin polycationic states of the N-methyl-substituted aza[14]metacyclophanes (R = Me in Fig. 1(b)), simply because the first oxidation process is already irreversible, and therefore the generated monocation was found to be decomposed immediately. Moreover, very recently, Bushby and co-workers showed that a fully N-aryl-

substituted aza[14]cyclophane (R = 2-methoxyphenyl in Fig. 1(b)) is oxidizable only up to two of four redox-active sites.6 This suggests that strong electrostatic repulsive interaction among the charged centers hinders generating the higher oxidized states for aza[14]cyclophane. As the best remedy for such an instability, it is quite effective that 4-aminophenyl groups are introduced on all the N-positions of aza[14]metacyclophanes. It is well known that para-phenylenediamine (PD) compounds can be readily converted by one-electron oxidation into stable semiquinone radical cations.7 Hence, 4-aminophenyl substituents afford stability of the generated radical cation due to the electron spin delocalization as well as lowering of the oxidation potential due to electron-donating ability of the amino group. In this communication, we report the electronic structures of fully dianisylaminophenylated aza[14]metacyclophanes (1), which can be easily oxidized into a spin-quintet tetra(radical cation).

The N-substituted aza[14]metacyclophane 1 was synthesized in 60% yield by using palladium-catalyzed aryl amination reaction between N-unsubstituted aza[14]metacyclophane 2 and N-4-bromophenyl-dianisylamine 3 (Scheme 1, see ESI†).

![Scheme 1 Synthesis of fully dianisylaminophenylated aza[14]metacyclophane.](Image)

Electrochemical oxidation of 1 by cyclic voltammetry (CV) displays four pairs of redox couples at oxidation potentials of $E_1 \approx -0.05$, $E_2 0.02$, $E_3 0.44$ and $E_4 0.57$ V vs Fc/Fc⁺ in CH₂Cl₂ as shown in Fig. 2. The corresponding first ($E_1$) and...
second (\(E_2\)) oxidation potentials for \(N,N',N'-\text{tetraanisyl-para-phenylenediamine}\) (TAPD) were −0.13 and 0.35 V under the same conditions. Each oxidation process was assigned as a two-electron process on the basis of the controlled potential coulometry (see ESI†), and this assignment was consistent with the following spectroelectrochemical studies. In the first oxidation process, two electrons are removed simultaneously from the two diagonally opposite PD moieties so as to reduce unfavorable electrostatic repulsion between the charged semi-quinoidal PD moieties. Note that the first oxidation of \(1\) inevitably proceeds to generation of dication even by treatment of a small portion of chemical oxidant. The remaining two neutral PD moieties in \(1^{2+}\) are also oxidized simultaneously to \(1^{3+}\) in the second oxidation process. In the third and fourth oxidation processes, the semi-quinoidal PD moieties in \(1^{3+}\) are further converted into the diamagnetic quinoidal PD moieties, leading to the highly charged states \(1^{4+}\) and \(1^{6+}\), respectively. All the oxidation processes were chemically reversible in both \(\text{CH}_2\text{Cl}_2\) and \(n\)-butyronitrile, whereas the currents of the last two oxidation waves gradually decreased by the consecutive potential cycling in \(\text{CH}_2\text{Cl}_2\), indicating the instability of \(1^{4+}\) and/or \(1^{6+}\) in \(\text{CH}_2\text{Cl}_2\) at room temperature. It should be noted that the first and second oxidations take place at almost the same potential. This means the feasibility of electron removal from \(1^{2+}\) to \(1^{4+}\), in contrast to the difficulty of oxidation from dication to tetracation in the fully \(N\)-aryl-substituted azah[14]cyclophane.\(^6\)

Fig. 2 Cyclic voltammogram of (a) \(1\) and (b) TAPD measured in \(\text{CH}_2\text{Cl}_2\) containing 0.1 M \(\text{n-Bu}_4\text{NBF}_4\) at 298 K (scan rate 0.1 V s\(^{-1}\)).

Fig. 3 UV-vis-NIR spectra of the stepwise electrochemical oxidation of \(1\) \(a\) in \(\text{CH}_2\text{Cl}_2/0.1\ M\ \text{n-Bu}_4\text{NBF}_4\) at room temperature: (a) \(1\) to \(1^{2+}\) (solid lines), (b) \(1^{2+}\) to \(1^{4+}\) (broken lines), and (c) \(1^{4+}\) to \(1^{6+}\) (dotted lines).

As a result of the (spectro-)electrochemical measurements, macrocycle \(1\) is anticipated to be converted to the di- or tetracation by the suitable oxidation treatment. To confirm the spin-multiplicity of \(1^{2+}\) and \(1^{4+}\), we measured continuous wave ESR (cw–ESR) spectra of the oxidized species of \(1\) treated with up to 2 or 4 molar equiv of tris(4-bromophenyl)aminium hexachloroantimonate at 195 K. Unfortunately, the definite fine-structured spectra\(^7\) characteristic of the spin-triplet (for \(1^{2+}\)) or spin-quintet state (for \(1^{4+}\)) were not observed in a frozen \(n\)-butyronitrile matrix at 123 K, whereas broad shoulders were seen beside the central resonance line (see ESI†). However, the forbidden...
$\Delta M_S = \pm 2$ resonance was detected in a half-field region of the allowed $\Delta M_S = \pm 1$ resonance, indicating the existence of high spin species. From the DFT calculations at the UB3LYP/3-21G level, the energy difference between the low-spin and high-spin states ($\Delta E_{S,T}$) for $1^{4+}$ was estimated to be small value of $-0.18$ kcal/mol, indicating that the high-spin triplet state is virtually degenerate with the competing low-spin singlet state. On the other hand, the ground state for $1^{4+}$ was anticipated to be spin-quintet state, judging from the estimated large $\Delta E_{T-Q}$ value of 13.7 kcal/mol. Corroborative evidence for the spin-multiplicity at low temperature was obtained for the generated $1^{3+}$ and $1^{4+}$ from the electron spin transient nutation (ESTN) measurements based on the pulsed ESR method (Fig. 4) (see ESI†). The ratio between the observed nutation frequency for $1^{3+}$ (and $1^{4+}$) and that for the spin-doublet species ($\sim 18$ MHz) was determined to be $\sqrt{2}$ (and 2), corresponding to the $|1, 0> \leftrightarrow |1, \pm 1>$ transition for spin-triplet state (and the $|2, \pm 1> \leftrightarrow |2, \pm 2>$ transition for spin-quintet state). In addition, the weak nutation signal for the $|2, 0> \leftrightarrow |2, \pm 1>$ transition was also observed at $\sim 45$ MHz for $1^{4+}$. Thus, this observation unequivocally establishes that the spin states for the generated $1^{3+}$ and $1^{4+}$ are in spin-triplet ($S = 1$) and spin-quintet ($S = 2$) states, respectively. In addition, the tetracation $1^{4+}$ was found to be stable under anaerobic condition at room temperature for several days, as indicated by no loss in the forbidden ESR signal intensity (for $\Delta M_S = \pm 2$ resonance).

Fig. 4 2D ESTN spectra of 1 in $n$-butyronitrile at 5K after addition of (a) 0.5 equiv and (b) 4 equiv of oxidant.

In summary, we have demonstrated that introduction of the dianisylaminophenyl groups into N-position to enable aza[1,2]metacyclophane oxidizable up to octacation, and the generated stable teta(cation radical) has the preference for high-spin alignment at low temperature in solution. The present toroidal molecular spin system may provide the possibility for extension to a larger two-dimensional molecular spin system.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental section and the electrochemical and spectroscopic data. See DOI: 10.1039/b000000x/
3 For the model compound for the 85 transition was also observed at $\sim 45$ MHz for $1^{4+}$. 20
13 For the model compound for 1, all the methoxy groups were replaced by the hydrogen atoms. Full geometry optimizations were carried out without any symmetrical constraint ($C_2$ symmetry). All the calculations were done with the Gaussian 03 program package.
Supplementary Information for:


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Synthesis of 1.

![Chemical structure of 1](image)

Anhydrous toluene (5 ml) was added into a mixture of 2 (125 mg, 0.26 mmol), 3 (1.73 g, 4.50 mmol), Pd(dba)\textsubscript{2} (8.0 mg, 0.014 mmol), Ph\textsubscript{3}FcP(\textit{t}-Bu)\textsubscript{2} [1] (19.1 mg, 0.027 mmol), and sodium \textit{tert}-butoxide (122 mg, 1.27 mmol) in a flask under argon, and the solution was heated to reflux for 74 h. After evaporation of the solvent, the residue was chromatographed on a silica gel (toluene/ethyl
acetate = 9:1 as eluent), and recrystallization from acetonitrile/ethyl acetate afforded 1 (262 mg, 60%) as a yellow solid: $^1$H NMR (400 MHz, acetone-$d_6$) $\delta$ 7.04 (d, $J = 8.7$ Hz, 8H), 6.97 (d, $J = 9.2$ Hz, 16H), 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), 6.36 (d, $J = 6.0$ Hz, 4H), 5.61 (s, 2H), 3.75 (s, 36H); $^{13}$C NMR (100 MHz, C$_6$D$_6$) $\delta$ 155.0, 154.4, 148.6, 143.0, 140.5, 139.6, 132.6, 127.8, 127.4, 124.6, 124.4, 121.4, 113.5, 107.3, 106.1, 98.6, 54.4, 53.6; FAB HRMS ($m$-nitrobenzyl alcohol) $m/z$ (relative intensity %) calcd for C$_{108}$H$_{96}$N$_8$O$_{12}$ [M]$^+$ 1696.7148, found 1696.7166 (88.1). Anal. Calcd for C$_{108}$H$_{96}$N$_8$O$_{12}$: C, 76.39; H, 5.70; N, 6.60; O, 11.31. Found: C, 75.05; H, 5.63; N, 6.33; O, 10.74.

Reference

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$^{-1}$).
Fig. S2. Controlled potential coulometry at 0.2 V vs Fc/Fc$^+$ for 1 (3.5 μmol) in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NBF$_4$ at 298 K. The net charge $Q$ was determined to be 1.26 C. Hence, 3.73 electrons (vertically four electrons) per molecule were removed at this potential. The same result was obtained by using $n$-butyronitrile as solvent [4.18 electrons were removed at the potential corresponding to the second oxidation process].
Fig. S3. CW-ESR spectra of I at 123 K after addition of (a) 2 equiv and (b) 4 equiv of oxidant.
**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 \(|S, M_S\rangle > \) to \(|S, M_S+1\rangle >\) can be expressed as 

\[
\omega_n = \left[ S(S+1) - M_S(M_S+1) \right]^{1/2} \omega_0
\]


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.