DOI: 10.1002/ange.201206831

A Polymacrocyclic Oligoarylamine with a Pseudobeltane Motif: Towards a Cylindrical Multispin System**

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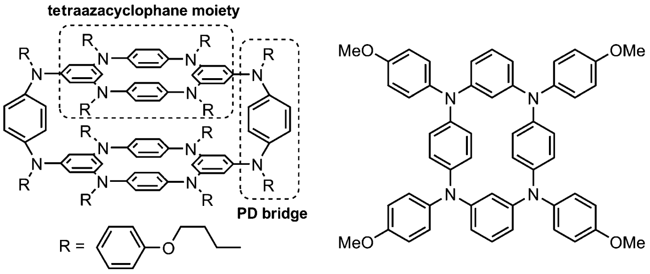
Although several types of belt-shaped compounds with novel structures have been reported over the past 30 years,[1] they are currently receiving increasing attention in conjunction with the synthesis of the shortest possible segments of single-walled carbon nanotubes.[2] Nanoscaled beltlike molecules are considered to be "cycles of cycles", and thus they have well-defined shapes with rigid cavities and can conceivably be used to construct solid-state materials with nanoporous networks. In addition, polymacrocycles with electron- (or hole-) delocalized (or localized) scaffolds are fascinating for potential applications towards electron (or hole) transport and/or as magnetic materials. In this context, oligoarylamine-based macrocyclic spin systems are being pursued to take advantage of the multi-electron redox properties of oligoarylamines and the relative stability of their poly(radical cation)s.[3–5] It is well known that strong Coulombic interactions between charged centers in oligoarylamine-based macrocycles hinder the generation of higher oxidation states with maximum spin multiplicity (Coulombic penalty).[6] As we have shown recently, however, the insertion of *para*-phenylenediamine (PD) units into the molecular backbone can alleviate the Coulombic penalty between charged triarylaminium radical centers in oligoarylamines and lower their oxidation potentials.[5]

Tetraaza[1_4]*m*,*p*,*m*,*p*-cyclophane, the smallest macrocyclic oligoarylamine bearing the alternating *meta–para* linkage, is transformed into an almost pure spin-triplet diradical dication upon two-electron oxidation.[7] Moreover, it has been demonstrated that the introduction of this macrocycle into a oligoarylamine backbone with one-dimensional connectivity can can convert the one-dimensional multispin system with a fragile spin-coupling pathway into a robust, aligned high-spin system.[8] Thus the polymacrocycles provided by the tetraazacyclophanes may be an indication for the further development of cylindrical multispin systems, which could culminate in nanotube-like surfaces with multi-electron redox activity. These findings led to the idea of utilizing the tetraazacyclophane unit as a component for a belt-shaped polymacrocyclic oligoarylamine. Polymacrocycle **1** (Scheme 1), which is classified as a pseudobeltane according to Vögtle's nomenclature,[1f,9] can be viewed as a kind of molecular belt containing six PD units connected by four 1,3,5-benzenetriyl ferromagnetic couplers,[10] and thereby the higher oxidation states of **1** can lead to multispin systems.



1 **4**

Scheme 1. The polymacrocyclic oligoarylamine **1** with a pseudobeltane structure and tetraaza[1_4]*m*,*p*,*m*,*p*-cyclophane **4** as a reference compound.

According to density functional theory (DFT) calculations for the model compound **1′**, in which the *n*-butoxy groups in **1** are replaced by hydrogen atoms for simplicity, at the B3LYP/6-31G* level, the optimized structure is a C_{2h}-symmetrical structure that closely resembles the X-ray structure of **1** (Figure 2).[11] The highest occupied molecular orbital (HOMO) and the next to highest molecular orbital ((HO-1)MO) is largely localized on the two PD bridges connecting two tetraazacyclophane moieties, whereas in the next highest orbitals, (HO-2)MO and (HO-3)MO, the electron density is mainly localized on the two tetraazacyclophane moieties (Figure 1). Moreover, as is apparent from the orbital energy diagram, the frontier MOs from HOMO to (HO-3)-MO are quasi-fourfold degenerate, so that a spin-quintet state can be anticipated in the tetracation $\mathbf{1}^{4+}$.

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[**] This work was supported by a Grant-in-Aid for Scientific Research (B) (24310090) from the Japan Society for the Promotion of Science (JSPS). D.S. thanks the JSPS Research Fellowship for Young Scientists.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201206831.

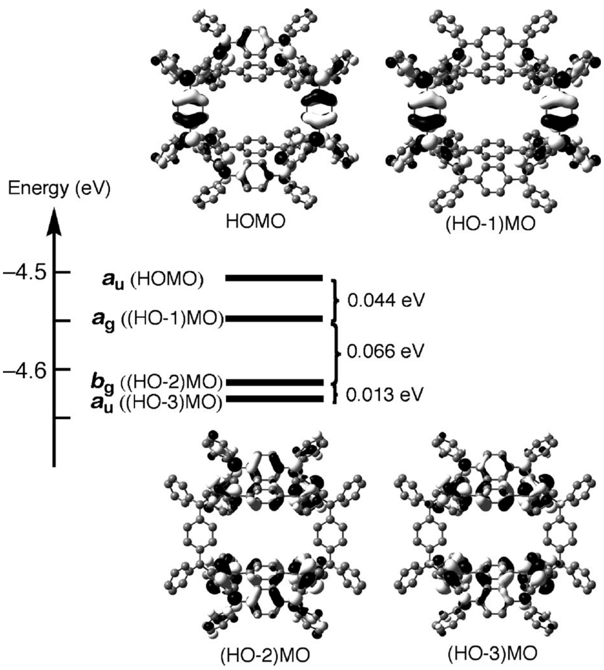
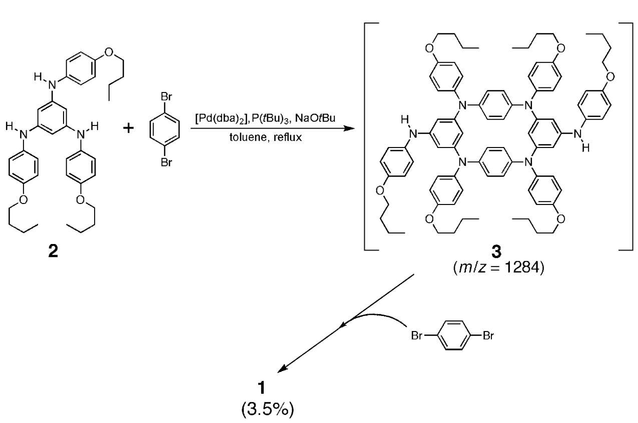


Figure 1. Frontier MOs for **1′** and their relative energy levels at the B3LYP/6-31G* level of theory.

The target molecule **1** was successfully prepared from 1,3,5-benzenetriamine **2**[12] and *p*-dibromobenzene in a one-pot manner by using the Buchwald–Hartwig cross-coupling amination reaction[13] (Scheme 2).[14] A solution of *p*-dibromobenzene in toluene was slowly added to a stirred mixture of **2**, P(tBu)$_3$, [Pd(dba)$_2$], and NaOtBu in toluene at 85 °C over 2 h, and the reaction mixture was stirred further at 85 °C. The reaction was monitored by MALDI-MS; the spectra exhibited an increase of a peak assigned not to **1** ($m/z = 2715$) but to a compound with a tetraazacyclophane framework **3** ($m/z = 1284$). After 5 h stirring, an additional solution of *p*-dibromobenzene in toluene was added to the stirred reaction mixture over 2 h, and subsequently the reaction mixture was stirred for a further 12 h at 85 °C. Finally, macrocyclization to **1** was confirmed by the appearance of a peak at $m/z = 2715$, and purification by silica gel column chromatography afforded **1** in 3.5 % yield as a white powder. Evidence of rigidity in the molecular structure appears in the ^{1}H and ^{13}C NMR spectra. Whereas only one singlet ^{1}H NMR signal is expected for the freely rotating *para*-phenylenes because of the highly symmetrical structure of **1**, a multiplet signal was observed for the corresponding protons attached to the *para*-phenylenes in the tetraazacyclophane moieties. In addition, the ^{13}C NMR spectrum of **1** also exhibits not 16-line but 17-line signals in the aromatic region, thus indicating that the free rotation of the *para*-phenylenes in the tetraazacyclophane moieties is prohibited even in solution at room temperature. In contrast, judging from the reported solution NMR spectra, free rotation of *para*-phenylene rings have been confirmed for the tetraazacyclophanes[7a,c] and their two-dimensionally expanded polymacrocycles.[4,5b]



Scheme 2. Synthesis of **1**. dba = *trans,trans*-dibenzylideneacetone.

As shown in Figure 2, direct information about the structure of **1** was obtained by X-ray crystallographic analysis of colorless needlelike single crystals grown from a mixed solution (benzene/*n*-hexane) (Table S1 in the Supporting Information).[15] In the crystal, each molecule of **1** possesses a crystallographic centrosymmetric point, and moreover, is associated with two benzene molecules and 1.5 *n*-hexane molecules, which penetrate the cavity (ca. 5 Å × 8 Å) formed between the two tetraazacyclophane macrocycles (Figure 2 b and c). In addition, two tetraazacyclophane moieties are sideslipped by 3 Å in parallel with each other in association with an inclination (56°) of the two PD bridges.

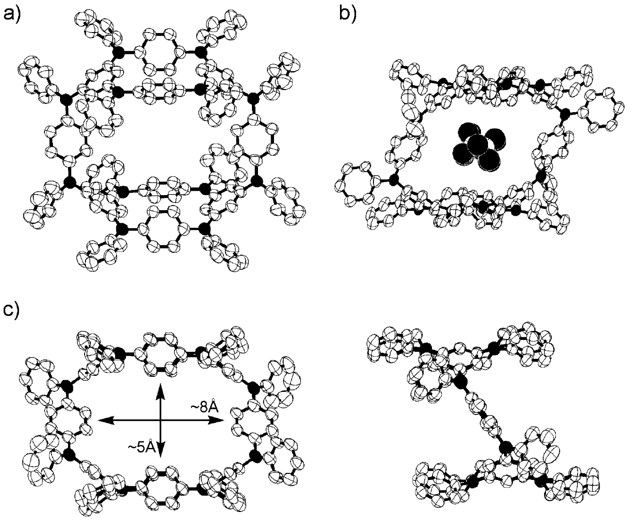


Figure 2. a) ORTEP representations of **1**. Crystallization solvent molecules (benzene and *n*-hexane), *n*-butoxy groups, and hydrogen atoms are omitted for clarity; nitrogen atoms are colored in black; ellipsoids are set at 50 % probability; b) another view including *n*-hexane; c) side views.

Electrochemical analysis of **1** indicated multi-electron redox activity originating from six PD units: quasi-two-electron transfer (−0.138 (2e) [V vs. Fc$^{0/+}$ (number of electrons)]); two one-electron transfers (+0.046 (1e) and +0.137 (1e)); quasi-two-electron transfer (+0.292 (2e)); quasi-four-electron transfer (+0.511 (2e), +0.560 (1e), and +0.598 (1e)); quasi-two-electron transfer (+0.666 (1e) and +0.702 (1e)). Thus, **1** can be oxidized up to a dodecacation on the cyclic and/or differential pulse voltammetric timescale (Figure 3). Under the same conditions, the oxidation potentials for the tetraazacyclophane **4** as a reference compound are −0.01 (1e), +0.22 (1e), +0.54 (1e), and +0.67 (1e).[5b] Therefore, it is deducible that removal of the first six electrons from **1** leads to the generation of six PD-based semiquinone radical cations, while the removal of further six electrons corresponds to the generation of six diamagnetic PD-based quinone dications.

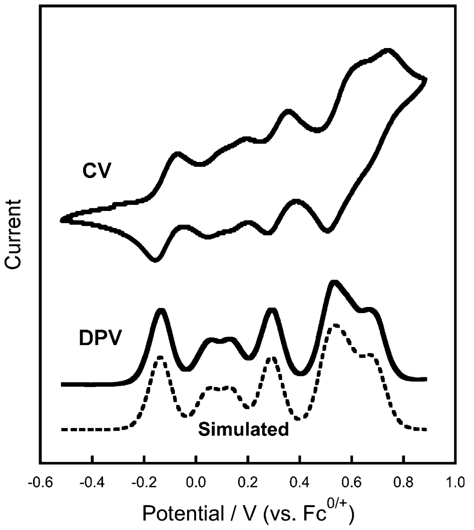


Figure 3. Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of **1**, measured in CH_2Cl_2 containing 0.1 M $n\mathrm{Bu_4NBF_4}$ at 298 K (scan rate 100 $\mathrm{mV\,s^{-1}}$). The simulated DPV[16] is drawn with a dotted line and the oxidation potentials were estimated by the DPV simulation (see text for details).

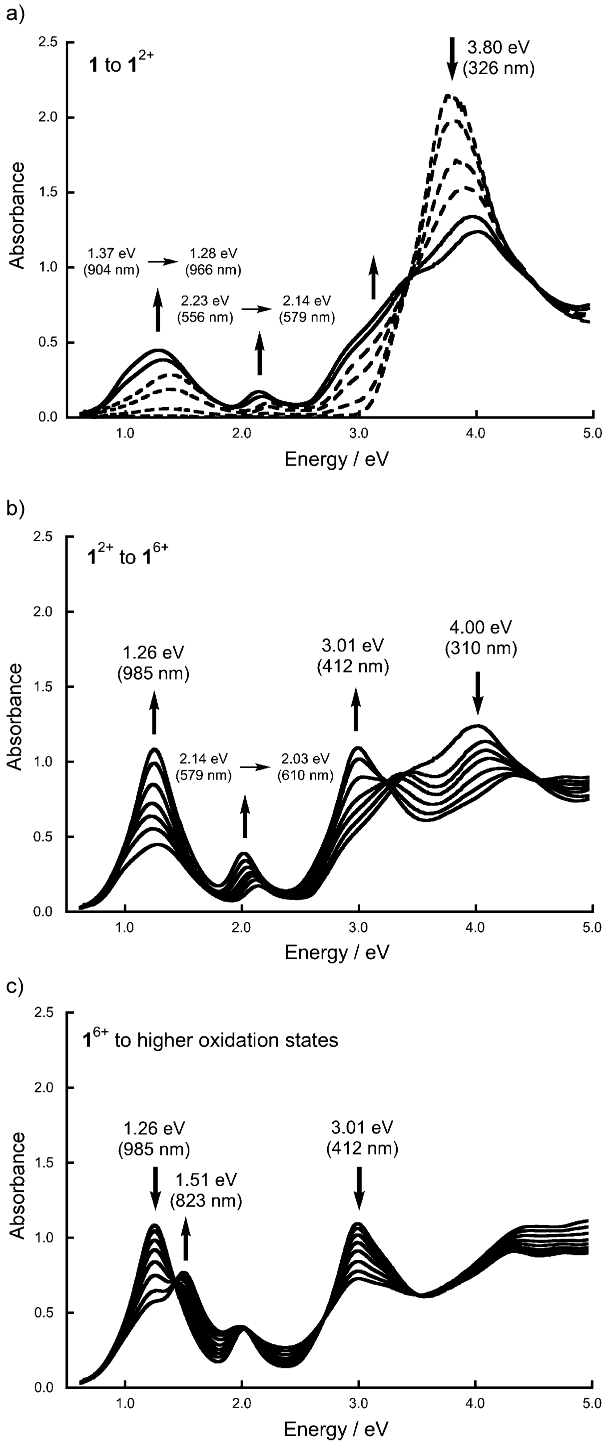


Figure 4. UV/Vis-NIR absorption spectra of the stepwise electrochemical oxidation of **1** in CH_2Cl_2 with 0.1 M $n\mathrm{Bu_4NBF_4}$ at 298 K: a) **1** to $\mathbf{1}^{2+}$; b) $\mathbf{1}^{2+}$ to $\mathbf{1}^{6+}$; c) further oxidation process from $\mathbf{1}^{6+}$.

To gain more insight into the electronic structure corresponding to each oxidation state indicated in the electrochemical study, we recorded changes in the absorption spectrum upon electrochemical oxidation of **1** to $\mathbf{1}^{6+}$ by using an optically transparent thin-layer electrochemical cell (Figure 4). As shown in Figure 4a, the growing lower energy bands at 1.37 eV ($\lambda_{max} = 904$ nm) and 2.23 eV ($\lambda_{max} = 556$ nm) for $\mathbf{1}^{+}$ were gradually red-shifted to 1.28 eV ($\lambda_{max} = 966$ nm) and 2.14 eV ($\lambda_{max} = 579$ nm) with an isosbestic point at 3.44 eV (360 nm) upon oxidation to $\mathbf{1}^{2+}$. This observation strongly suggests that the radical cation $\mathbf{1}^{+\bullet}$ can be generated by treatment with less than one equiv of an oxidant, although the first oxidation process can be considered to be a two-electron transfer process based on the present electrochemical study. Further oxidation into $\mathbf{1}^{6+}$ was accompanied by the continuous increase in intensity of the lowest energy band which is assignable to the charge-resonance (CR) intervalence (IV) band originating from generation of the semiquinone radical cation in the PD unit.[17] Finally the absorbance intensity reached up to about thrice that of $\mathbf{1}^{2+}$, thus indicating that all the PD moieties were converted to the corresponding semiquinone radical cations (Figure 4b). When $\mathbf{1}^{6+}$ was oxidized further, the intense CR IV band rapidly decreased together with the higher energy band at 3.01 eV ($\lambda_{max} = 412$ nm), which had been observed for $\mathbf{1}^{6+}$ (Figure 4b), and simultaneously, a new band at 1.51 eV ($\lambda_{max} = 823$ nm) grew with two isosbestic points [1.44 eV (863 nm) and 2.70 eV (460 nm)]. This new band corresponds to the conversion from the semiquinoidal radical cation into the diamagnetic quinoidal dication in the PD units (Figure 4c).

The solution ESR spectrum of $\mathbf{1}^+$ generated by chemical oxidation with 0.5 equivalents of tris(4-bromophenyl)aminium hexachloroantimonate (Magic Blue)[18] in CH_2Cl_2 at 295 K exhibited a multiplet hyperfine structure at $g = 2.0029$ (Figure S2a in the Supporting Information). The observed spectrum was reasonably reproduced by the following hyperfine coupling (hfc) constants: $a_{N1} = 0.250$ mT (4N) and $a_{N2} = 0.035$ mT (8N), and the contribution from unresolved hydrogen nuclei was assumed to be incorporated in the linewidth of the spectrum simulation (0.20 mT) (Figure S2b), indicating that the spin density resides mainly on the two PD bridges (Figure 5 a). However, on closer inspection of the spin-density distribution over the tetraazacyclophane moieties in $\mathbf{1}'^+$ (Figure 5 a) we found that no spin density is distributed on the inner PD units, whereas a part of the spin density is on the outer PD units, probably originating from the sideslipped structure of **1** (Figures 1c and 5b).[11] Indeed, these findings were reflected in the temperature dependence of the observed ESR spectrum (Figure 6 a). The hyperfine structure for $\mathbf{1}^+$ became vague with decreasing temperature, and we found that such a spectral change is reproducible only by considering a windshield-wiper-like motion interconverting two sideslipped structures with a rate constant k (Figure 5 b). The rate constants at various temperatures were determined by spectral simulations of the observed ESR spectra by using the ESR-EXN program on the basis of the stochastic Liouville method (Figure 6 b).[19] In the measured temperature range, plots of $\ln(k)$ versus $1/T$ gave a linear relationship, thus indicating an Arrhenius-type temperature dependence [$k = A\exp(-\Delta G^*/k_B T)$, where k_B is the Boltzmann constant] (Figure S3). Consequently, from the Arrhenius plots, the barrier to thermal interconversion between two sideslipped structures, ΔG^*, and the prefactor A were estimated to be 5.0 kcal mol^{-1} and 2.3×10^{11} s^{-1}, respectively.

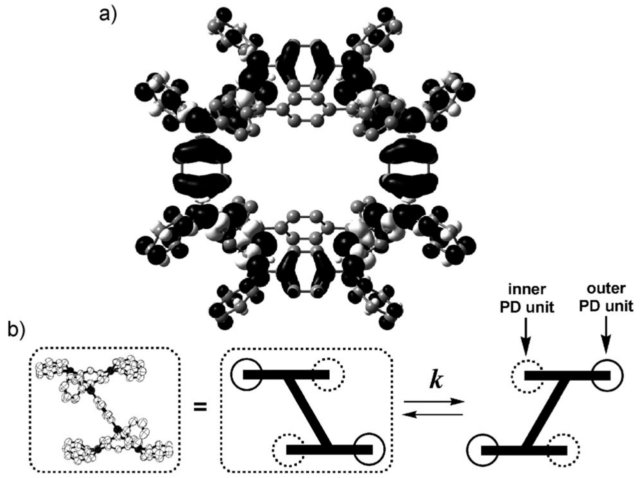


Figure 5. a) Spin-density distribution of $\mathbf{1}'^+$ (UB3LYP/6-31G*; black: positive spin, white: negative spin; spin isosurface value = 0.0003 electron au^{-3}), and b) a windshield-wiper-like interconversion between two sideslipped structures at a rate constant k.

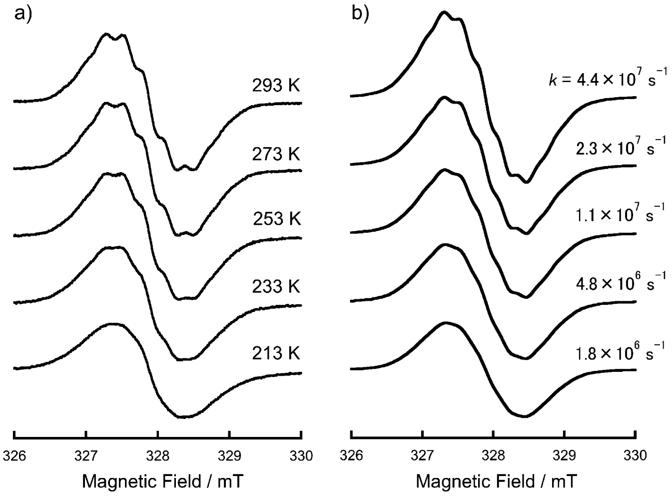


Figure 6. a) Temperature-dependent ESR spectra of $\mathbf{1}^+$ in CH_2Cl_2 and b) the simulated spectra.

The electrochemical and spectroelectrochemical studies of **1** (Figures 3 and 4) indicate that the dicationic, tetracationic, and hexacationic species are accessible by appropriate chemical oxidation, and therefore, their spin multiplicities at low temperatures are of great interest in view of the realization of cylindrical multispin systems. Polycations $\mathbf{1}^{2+}$ and $\mathbf{1}^{4+}$ were readily generated by adding 2 and 4 equivalents of Magic Blue at 195 K in CH_2Cl_2. However, treatment of **1** with 6 or more equivalents of Magic Blue did not generate $\mathbf{1}^{6+}$. At this stage, we did not search for oxidizing agents suitable for the generation of $\mathbf{1}^{6+}$. Information about the spin multiplicities at 5 K for $\mathbf{1}^{2+}$ and $\mathbf{1}^{4+}$ were unequivocally obtained by pulsed ESR spectroscopy detecting the electron spin transient nutation (ESTN) signal.[20] As is apparent from Figure 7 a and Table 1, the nutation signal of 25.4 MHz can be assigned to the spin-triplet state of $\mathbf{1}^{2+}$, judging from the nutation signal (18.6 MHz) due to the spin-doublet impurity. Note that no noticeable zero-field splitting was observed in the nutation signal for the spin-triplet $\mathbf{1}^{2+}$, indicating that the average distance between the two unpaired electrons is quite great. In fact, it is anticipated that the quasi-degenerate HOMO and (HO-1)MO of $\mathbf{1}'$ (Figure 1) can be regarded as two singly occupied MOs in $\mathbf{1}'^{2+}$, and thus, the two unpaired electrons are mainly distributed over two PD linkers, which are separated by 12.83 Å according to the X-ray structure (Figure 2). Concomitantly, we observed the nutation signals of 30.6 and 36.2 MHz due to the spin-quartet state of $\mathbf{1}^{3+}$, which is generated simply because of a slight excess of Magic Blue. In contrast, the ESTN spectrum for the polycationic species generated by treatment with 4 equivalents of Magic Blue clearly demonstrated the existence of an almost pure spin-quintet state of $\mathbf{1}^{4+}$.[21] The two nutation signals of 27.8 and 35.5 MHz indicate $S = 2$ spin multiplicity of $\mathbf{1}^{4+}$, since only a very weak signal corresponding to the excited triplet state of $\mathbf{1}^{4+}$ was detected at 20.0 MHz (Figure 7b and Table 1). This result indicates that $\mathbf{1}^{4+}$ is in a spin-quintet state at 5 K and the excited spin-triplet state is readily accessible owing to the very small energy spacing, and thus four unpaired electrons are accommodated separately in the two PD bridges and the two

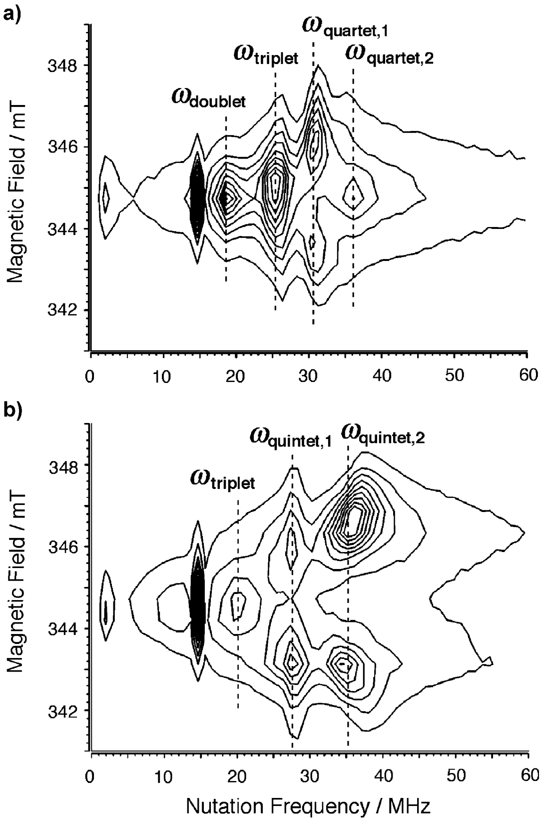


Figure 7. Two-dimensional ESTN spectra of **1** in CH_2Cl_2 at 5 K after addition of a) 2 equiv and b) 4 equiv of Magic Blue.

Table 1: Spectroscopic data of the ESTN spectroscopy for $\mathbf{1}^{2+}$ and $\mathbf{1}^{4+}$.

Species	Observed nutation frequency [MHz][a]	Transition assignment
$\mathbf{1}^{2+}$	25.4 ($\omega_t=\sqrt{2}\ \omega_d$)	$\lvert 1, \pm 1\rangle \Leftrightarrow \lvert 1, 0\rangle$
doublet impurity	18.6 (ω_d)	$\lvert 1/2, +1/2\rangle \Leftrightarrow \lvert 1/2, -1/2\rangle$
quartet impurity	30.6 ($\omega_{q,1}=\sqrt{3}\ \omega_d$)	$\lvert 3/2, \pm 3/2\rangle \Leftrightarrow \lvert 3/2, \pm 1/2\rangle$
	36.2 ($\omega_{q,2}=2\ \omega_d$)	$\lvert 3/2, +1/2\rangle \Leftrightarrow \lvert 3/2, -1/2\rangle$
$\mathbf{1}^{4+}$	27.8 ($\omega_{quintet,1}=\sqrt{2}\ \omega_t$)	$\lvert 2, \pm 2\rangle \Leftrightarrow \lvert 2, \pm 1\rangle$
	35.5 ($\omega_{quintet,2}=\sqrt{3}\ \omega_t$)	$\lvert 2, \pm 1\rangle \Leftrightarrow \lvert 2, 0\rangle$
excited triplet	20.0 (ω_t)	$\lvert 1, \pm 1\rangle \Leftrightarrow \lvert 1, 0\rangle$

[a] d = doublet, t = triplet, q = quartet.

tetraazacyclophane moieties, as is expected from the HOMO to (HO-3)MOs on **1**′ (Figure 1).

In summary, the newly prepared pseudobeltane-like polymacrocyclic oligoarylamine **1** displays multi-electron redox activity up to the electrochemical generation of dodecacation, and moreover, the diradical dication $\mathbf{1}^{2+}$ and tetraradical tetracation $\mathbf{1}^{4+}$ generated by chemical oxidation were found to be in high-spin states at low temperatures. In addition, dynamic ESR spectroscopy revealed the thermally activated interconversion between two sideslipped structures in radical cation $\mathbf{1}^{+}$. The present toroidal multispin system is thus expected to serve as a useful building block in the extension to cylindrical multispin systems, which we are now actively pursuing.

Received: August 23, 2012

Keywords: arylamines · cyclophanes · electrochemistry · ESR spectroscopy · radical ions

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[21] As pointed out by one of the reviewers, it is important to quantify the fraction of the generated tetracationic species of **1** in CH_2Cl_2 solution. As shown in the Suppoting Information (Figure S4), we have confirmed the quantitative generation of $\mathbf{1}^{4+}$ by chemical oxidation of bis(trifluoroacetoxy)iodobenzene (PIFA), which is one of the diamagnetic one-electron oxidizing agents [L. Eberson, M. F. Hartshorn, O. Persson, *Acta Chem. Scand.* **1995**, *49*, 640], in comparison with a stable monoradical (2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)) as a reference, and the solution exhibited the same ESTN spectrum at 5 K (Figure 7b). The tetracation $\mathbf{1}^{4+}$ was found to be stable in solution under inert atmosphere at room temperature for three months or longer. However, we failed to isolate the salt of $\mathbf{1}^{4+}$ which shows a satisfactory elemental analysis, probably due to partial decomposition.