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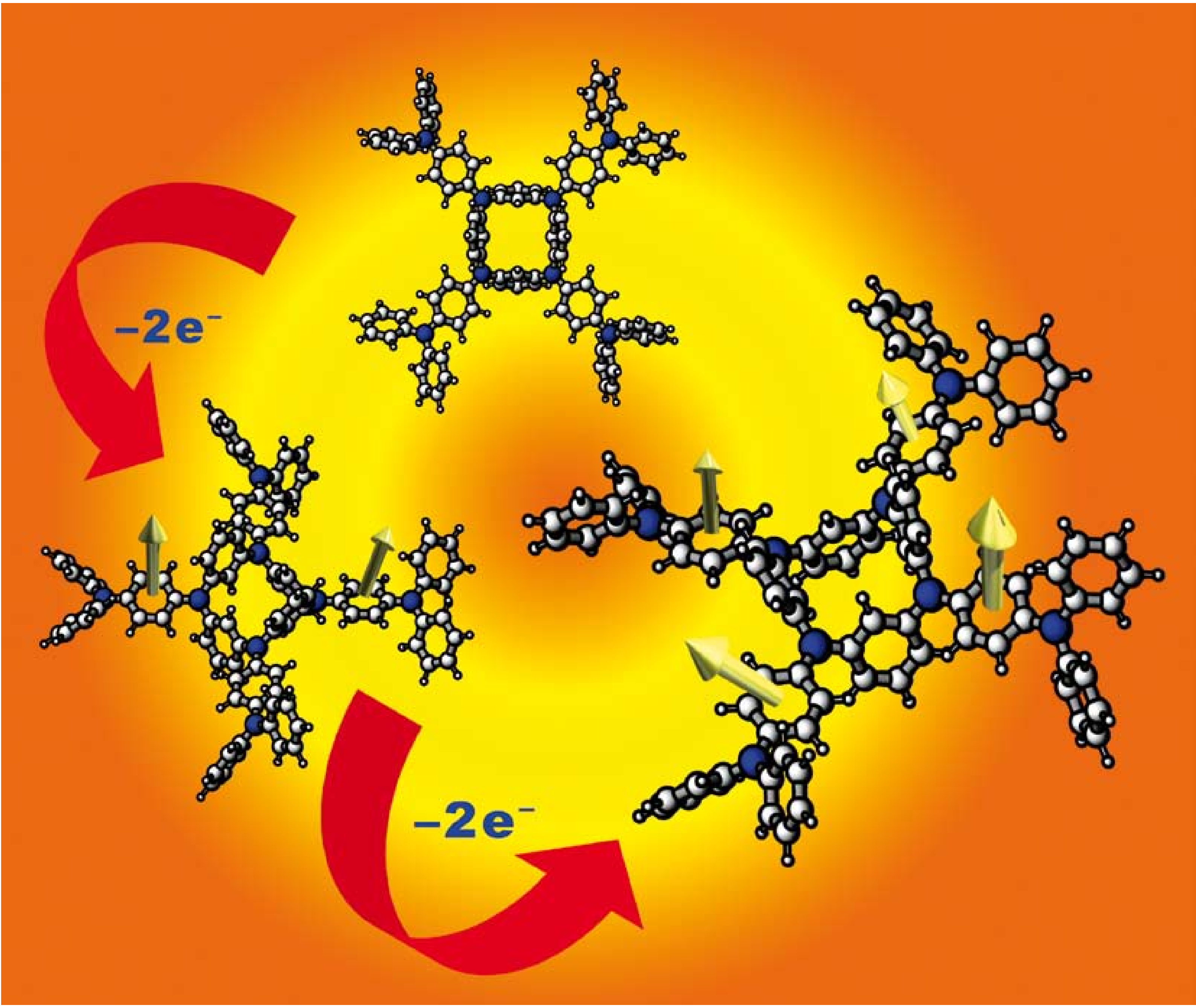

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An *N*-substituted aza[1_4]metacyclophane tetracation: a spin-quintet tetraradical with four *para*-phenylenediamine-based semi-quinone moieties†

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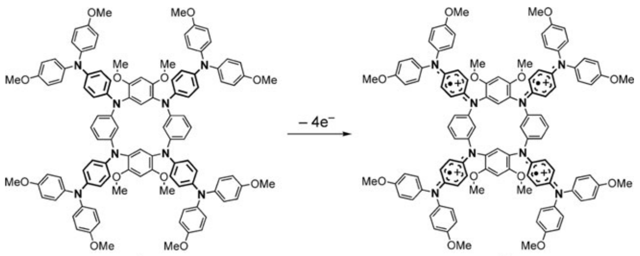
A fully dianisylaminophenylated aza[1_4]metacyclophane has been synthesized that exhibits four reversible two-electron oxidation processes, and its dicationic and tetracationic species have been found to be in spin-triplet and spin-quintet states.

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

However, as exemplified by our previous studies,[2] it proved impossible to realize the high-spin polycationic states of an *N*-methyl-substituted aza[1_n]metacyclophane (Fig. 1(b); R = Me), simply because the first oxidation process was irreversible, and therefore the generated monocation decomposes immediately. Moreover, very recently, Bushby and co-workers showed that only up to two of the four redox-active sites in a fully *N*-aryl-substituted aza[1_4]metacyclophane (Fig. 1(b); R = 2-methoxyphenyl) were oxidizable.[6] This suggests that strong electrostatic repulsive interactions among the charged sites hinder generation of the higher oxidation states of aza[1_4]metacyclophanes. As the best remedy for such instability, the introduction of 4-aminophenyl groups at all the *N*-positions of aza[1_n]metacyclophanes is quite effective. It is well known that *para*-phenylenediamine (PD) compounds can be readily converted by a one-electron oxidation into stable semiquinone radical cations.[7] Hence, 4-aminophenyl substituents afford stability to the generated radical cation due to electron spin delocalization, as well as by lowering the oxidation potential due to the electron-donating ability of the amino group. In this Communication, we report the electronic structure of a fully dianisylaminophenylated aza[1_4]metacyclophane, **1**, which can be easily oxidized to a spin-quintet tetra(radical cation).



1 **1^{4+}**

The *N*-substituted aza[1_4]metacyclophane, **1**, was synthesized in 60% yield by performing a palladium-catalyzed aryl amination reaction between an *N*-unsubstituted aza[1_4]metacyclophane, **2**,[8] and *N*-4-bromophenyl-dianisylamine (**3**) (Scheme 1, see ESI†).

The electrochemical oxidation of **1** by cyclic voltammetry (CV) displayed four pairs of redox couples at oxidation potentials of $E_1 \sim -0.05$, $E_2 = 0.02$, $E_3 = 0.44$ and $E_4 = 0.57$ V *vs.* Fc/Fc$^+$ in CH_2Cl_2, as shown in Fig. 2. The corresponding first (E_1) and second (E_2) oxidation potentials

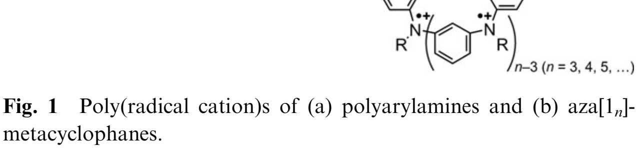


Fig. 1 Poly(radical cation)s of (a) polyarylamines and (b) aza[1_n]-metacyclophanes.

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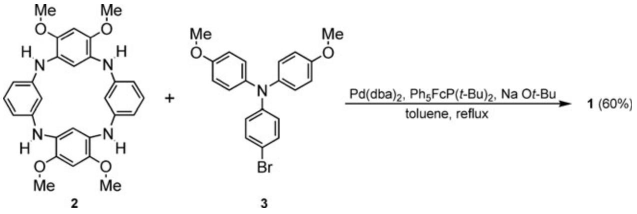
† Electronic supplementary information (ESI) available: Experimental section, and the electrochemical and spectroscopic data. See DOI: 10.1039/b805333b



Scheme 1 Synthesis of fully dianisylaminophenylated aza[1_4]metacyclophane **1**.

for *N*,*N*,*N*′,*N*′-tetraanisyl-*para*-phenylendiamine (TAPD) were −0.13 and 0.35 V, respectively, 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 repulsions between the charged semi-quinoidal PD moieties. Note that the first oxidation of **1** inevitably proceeds to generate a dication, even when treated with small portions of chemical oxidant. The remaining two neutral PD moieties in $\mathbf{1}^{2+}$ are also oxidized simultaneously, to generate $\mathbf{1}^{4+}$ in the second oxidation process. In the third and fourth oxidation processes, the semi-quinoidal PD moieties in $\mathbf{1}^{4+}$ are further converted into the diamagnetic quinoidal PD moieties, leading to the highly charged states $\mathbf{1}^{6+}$ and $\mathbf{1}^{8+}$, respectively. All the oxidation processes were chemically reversible in both CH_2Cl_2 and *n*-butyronitrile, whereas the currents of the last two oxidation waves gradually decreased upon consecutive potential cycling in CH_2Cl_2, indicating the instability of $\mathbf{1}^{6+}$ and/or $\mathbf{1}^{8+}$ in CH_2Cl_2 at room temperature. It should be noted that the first and second oxidations take place at almost the same potential, indicating the feasibility of electron removal from $\mathbf{1}^{2+}$ to $\mathbf{1}^{4+}$. This fact contrasts strikingly with the difficulty of oxidising the dication to the tetracation in the fully *N*-aryl-substituted aza[1_4]metacyclophane.[6]

Fig. 3 reveals evolution of the absorption spectrum during the course of the oxidation of **1** by the use of an optically-transparent thin-layer electrochemical cell. During the oxidation process of **1** to $\mathbf{1}^{2+}$, a relatively broad absorption band grew at 982 nm (Fig. 3(a)). This band is known as the intervalence (IV) band, and is attributable to the electron spin delocalized state (semi-quinone) within the PD radical cation.[7] Note that the observed absorbance of $\mathbf{1}^{2+}$ is twice as intense as that of the radical cation of TAPD, the reference compound of **1**, measured under the same conditions. This observation supports that the first oxidation process corresponds to a two-electron process. Further oxidation of $\mathbf{1}^{2+}$ leads to a continuous increase in absorbance for the IV band, up to nearly twice that of $\mathbf{1}^{2+}$ (Fig. 3(b)). This strongly indicates that the tetra(radical cation) of **1** is formed by a four-electron oxidation. More noteworthy is the fact that the absorbance in the low-energy region of the intense IV band decreases, with an isosbestic point at 1250 nm, on going from $\mathbf{1}^{2+}$ to $\mathbf{1}^{4+}$. Judging from the fact that a weak IV charge transfer band *via* the *meta*-phenylene is generally observed in the near infrared (NIR) region,[9] it is suggested that the absorption in the low-energy region of the IV band of $\mathbf{1}^{2+}$ corresponds to spin hopping transfer between the oxidized and neutral PD units in $\mathbf{1}^{2+}$.[10] This phenomenon is quite interesting in relation to the concerted two-electron transfer processes in mixed-valence molecules with a square topology.[11] When $\mathbf{1}^{2+}$ is oxidized to $\mathbf{1}^{4+}$, the spin-transferable sites disappear, and hence the low-energy region of the intense IV band also disappear. Furthermore, this intense IV band begins to decrease rapidly when $\mathbf{1}^{4+}$ is further oxidized, and new absorptions at $\lambda_{\max} = 665$ and 765 nm emerge, with an isosbestic point at 825 nm corresponding to a conversion from the semi-quinoidal PD to the quinoidal PD (Fig. 3(c)).

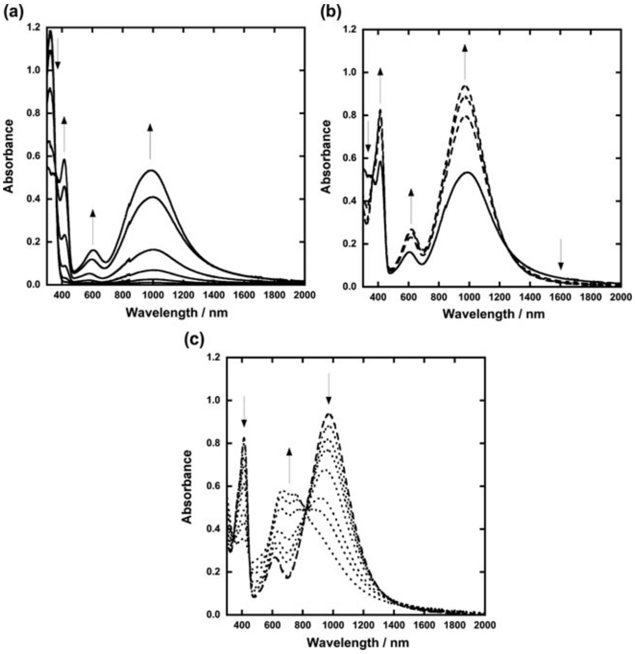


Fig. 3 UV-vis–NIR spectra of the stepwise electrochemical oxidation of **1** in CH_2Cl_2/0.1 M *n*-Bu_4NBF_4 at room temperature: (a) **1** to $\mathbf{1}^{2+}$ (—), (b) $\mathbf{1}^{2+}$ to $\mathbf{1}^{4+}$ (--) and (c) $\mathbf{1}^{4+}$ to $\mathbf{1}^{6+}$ (···).

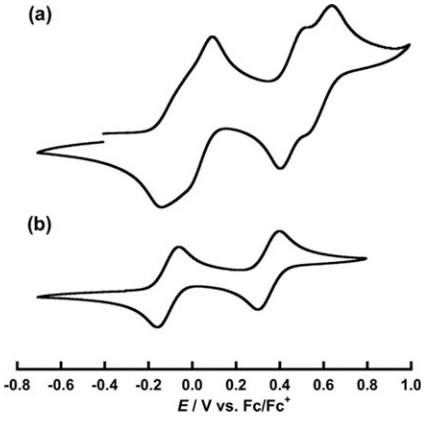


Fig. 2 Cyclic voltammograms of (a) **1** and (b) TAPD, measured in CH_2Cl_2 containing 0.1 M *n*-Bu_4NBF_4 at 298 K (scan rate 0.1 V s^{-1}).

As a result of these spectroelectrochemical measurements, macrocycle **1** is anticipated to be converted to its di- or tetracation by a suitable oxidation treatment. To confirm the spin multiplicity of $\mathbf{1}^{2+}$ and $\mathbf{1}^{4+}$, we measured continuous wave ESR (cw-ESR) spectra of the oxidized species of **1**,

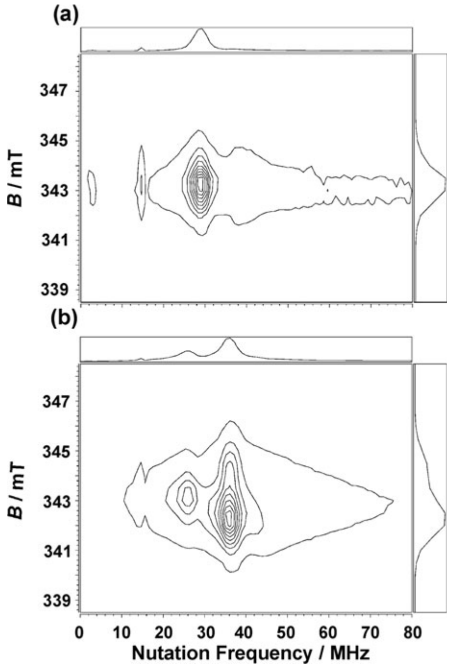


Fig. 4 2D ESTN spectra of **1** in *n*-butyronitrile at 5 K after the addition of (a) 0.5 equiv. and (b) 4 equiv. of oxidant.

treated with up to 2 or 4 molar equiv. of tris(4-bromophenyl)-aminium hexachloroantimonate at 195 K. Unfortunately, definitive fine-structured spectra[12] characteristic of a spin-triplet (for $\mathbf{1}^{2+}$) or a spin-quintet (for $\mathbf{1}^{4+}$) state were not observed in a frozen *n*-butyronitrile matrix at 123 K; instead, 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.[12] From DFT calculations at the UB3LYP/3-21G level,‡ the energy difference between the low-spin and high-spin states ($\Delta E_{S\text{–}T}$) for $\mathbf{1}^{2+}$ was estimated to be only −0.18 kcal mol^{-1}, indicating that the high-spin triplet state is virtually degenerate with the competing low-spin singlet state. On the other hand, judging from the estimated large $\Delta E_{T\text{–}Q}$ value of 13.7 kcal mol^{-1}, the ground state for $\mathbf{1}^{4+}$ was anticipated to be a spin-quintet state. Corroborative evidence for the spin-multiplicity of $\mathbf{1}^{2+}$ and $\mathbf{1}^{4+}$ at low temperatures was obtained by electron spin transient nutation (ESTN) measurements based on the pulsed ESR method (Fig. 4) (see ESI†). The ratio between the observed nutation frequency for $\mathbf{1}^{2+}$ (and $\mathbf{1}^{4+}$) and that for the spin-doublet species (~18 MHz) was determined to be $\sqrt{2}$ (and 2), corresponding to the $|1, 0\rangle \Leftrightarrow |1, \pm1\rangle$ transition for the spin-triplet state (and to the $|2, \pm1\rangle \Leftrightarrow |2, \pm2\rangle$ transition for the spin-quintet state). In addition, a weak nutation signal for the $|2, 0\rangle \Leftrightarrow |2, \pm1\rangle$ transition was also observed at ~45 MHz for $\mathbf{1}^{4+}$. This observation therefore unequivocally establishes that the spin states for the generated $\mathbf{1}^{2+}$ and $\mathbf{1}^{4+}$ are spin-triplet ($S = 1$) and spin-quintet ($S = 2$), respectively. In addition, tetracation $\mathbf{1}^{4+}$ was found to be stable under anaerobic conditions at room temperature for several days, as indicated by there being no loss in the forbidden ESR signal intensity (for the $\Delta M_S = \pm 2$ resonance).

In summary, we have demonstrated that introduction of dianisylaminophenyl groups at the *N*-positions of an aza[1_4]-metacyclophane enable it to be oxidized up to an octacation, and the generated stable tetra(radical cation) has a preference for high-spin alignment at low temperature in solution. The present toroidal molecular spin system may provide the possibility for its extension to a larger 2D molecular spin system.

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Notes and references

‡ For the model compound of **1**, all the methoxy groups were replaced by hydrogen atoms. Full geometry optimizations in C_2 symmetry were carried out for all the oxidized states of the model compound. All calculations were performed using the Gaussian 03 program package.

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