

N-substituted aza[1₄]metacyclophane tetracation: a spin–quintet tetraradical having four *para*-phenylenediamine-based semi-quinone moieties†

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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 [1_{*n*}]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 [1_{*n*}]metacyclophanes (or aza[1_{*n*}]metacyclophanes), and reported the preparation and properties of a series of aza[1_{*n*}]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, polyarylamine, in which *meta*-phenylenes are connected by nitrogen-bridging units, can be expected to become high-spin materials possessing the generated aminium 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[1_{*n*}]metacyclophanes can be regarded as intriguing candidates for the toroidal molecular spin systems. In the polyarylmethyl-based polyradicals, calix[4]arene-based macrocyclic high-spin molecules has already been reported.⁵

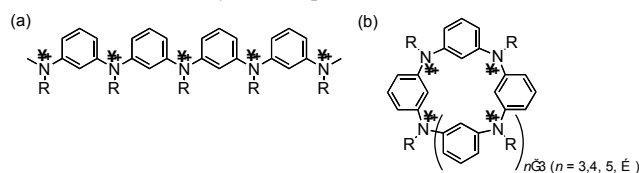
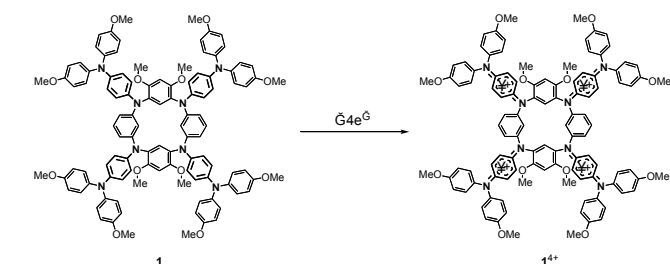


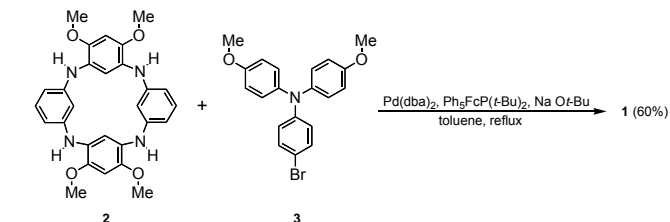
Fig. 1 Poly(radical cation)s of (a) polyarylamine and (b) aza[1_{*n*}]metacyclophane.

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[1_{*n*}]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[1_{*n*}]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**⁸ and *N*-4-bromophenyldianisylamine **3** (Scheme 1, see ESI†).



Scheme 1 Synthesis of fully dianisylaminophenylated aza[1₄]metacyclophane.

Electrochemical oxidation of **1** by cyclic voltammetry (CV) displays 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 CH₂Cl₂ as shown in Fig. 2. The corresponding first (E_1) and

second (E_2) oxidation potentials for N,N,N',N' -tetraanisyl-*para*-phenyldiamine (TAPD) were -0.13 and 0.35 V under the same conditions. Each oxidation process was assigned as 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 small portion of chemical oxidant. The remaining two neutral PD moieties in $\mathbf{1}^{2+}$ are also oxidized simultaneously to $\mathbf{1}^{4+}$ 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 by the 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. This means the feasibility of electron removal from $\mathbf{1}^{2+}$ to $\mathbf{1}^{4+}$, in contrast to the difficulty of oxidation from dication to tetracation in the fully *N*-aryl-substituted aza[14]cyclophane.⁶

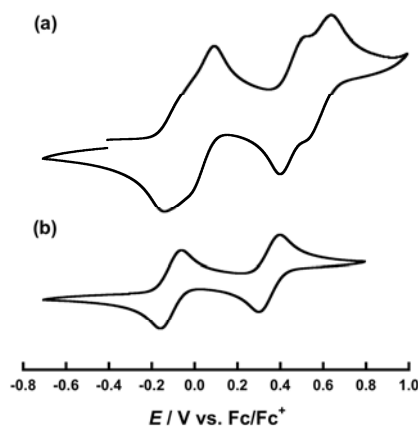


Fig. 2 Cyclic voltammogram of (a) **1** and (b) TAPD measured in CH_2Cl_2 containing 0.1 M *n*-Bu₄NBF₄ at 298 K (scan rate 0.1 V s⁻¹).

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

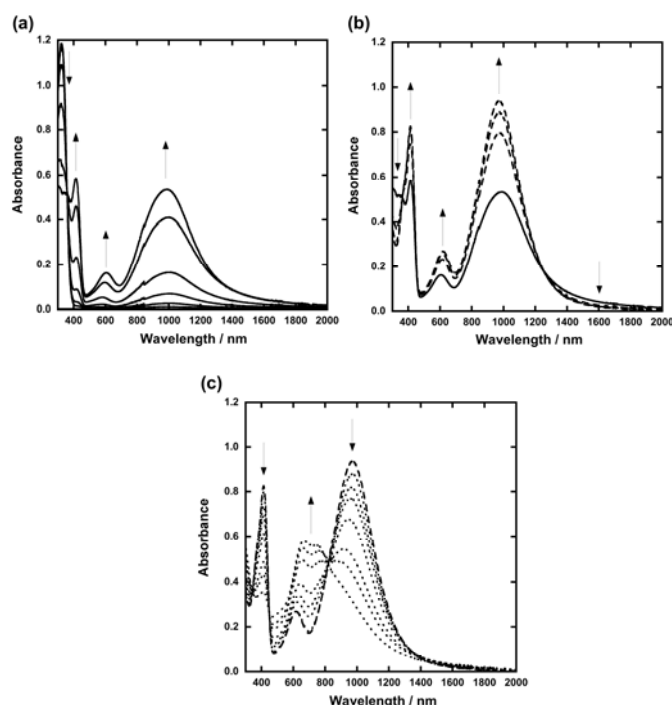


Fig. 3 UV-vis-NIR spectra of the stepwise electrochemical oxidation of **1** in $\text{CH}_2\text{Cl}_2/0.1$ M *n*-Bu₄NBF₄ at room temperature: (a) **1** to $\mathbf{1}^{2+}$ (solid lines), (b) $\mathbf{1}^{2+}$ to $\mathbf{1}^{4+}$ (broken lines), and (c) $\mathbf{1}^{4+}$ to $\mathbf{1}^{6+}$ (dotted 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 $\mathbf{1}^{2+}$ and $\mathbf{1}^{4+}$, 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 characteristic of the spin-triplet (for $\mathbf{1}^{2+}$) or spin-quintet state (for $\mathbf{1}^{4+}$) 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.¹² From the DFT calculations at the UB3LYP/3-21G level,¹³ the energy difference between the low-spin and high-spin states (ΔE_{S-T}) for 1^{2+} 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 ΔE_{T-Q} value of 13.7 kcal/mol. Corroborative evidence for the spin-multiplicity at low temperature was obtained for the generated 1^{2+} 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^{2+} (and 1^{4+}) and that for the spin-doublet species (~ 18 MHz) was determined to be $\sqrt{2}$ (and 2), corresponding to the $|1, 0\rangle \leftrightarrow |1, \pm 1\rangle$ transition for spin-triplet state (and the $|2, \pm 1\rangle \leftrightarrow |2, \pm 2\rangle$ transition for spin-quintet state). In addition, the weak nutation signal for the $|2, 0\rangle \leftrightarrow |2, \pm 1\rangle$ transition was also observed at ~ 45 MHz for 1^{4+} . Thus, this observation unequivocally establishes that the spin states for the generated 1^{2+} 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).

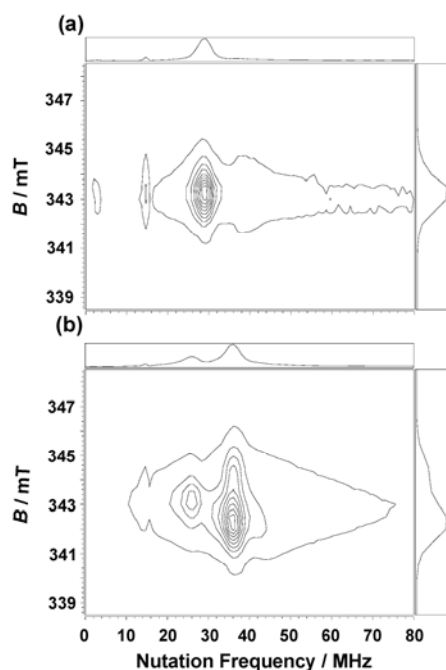


Fig. 4 2D ESTN spectra of **1** in *n*-butyronitrile at 5K after addition of (a) 0.5 equiv and (b) 4 equiv of oxidant.

In summary, we have demonstrated that introduction of the dianisylaminophenyl groups into *N*-position to enable aza[14]metacyclophane oxidizable up to octacation, and the generated stable tetra(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/
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- 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:

***N*-substituted aza[1₄]metacyclophane tetracation: a spin quintet tetraradical having four *para*-phenylenediamine-based semi-quinone moieties**

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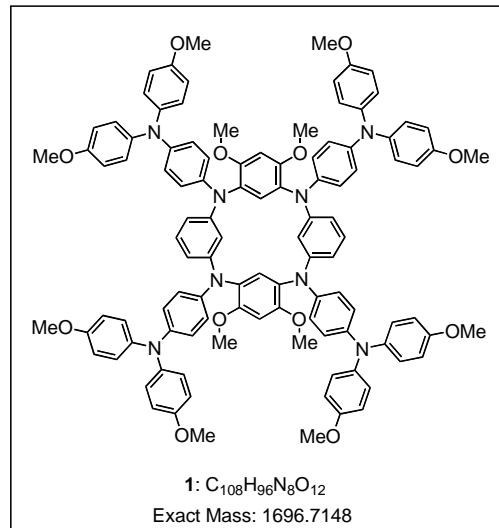
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Synthesis of 1.



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)₂ (8.0 mg, 0.014 mmol), Ph₅FcP(*t*-Bu)₂ [1] (19.1 mg, 0.027 mmol), and sodium *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: ^1H NMR (400 MHz, acetone- d_6) δ 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_6D_6) δ 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 $\text{C}_{108}\text{H}_{96}\text{N}_8\text{O}_{12}$ $[\text{M}]^+$ 1696.7148, found 1696.7166 (88.1). Anal. Calcd for $\text{C}_{108}\text{H}_{96}\text{N}_8\text{O}_{12}$: 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

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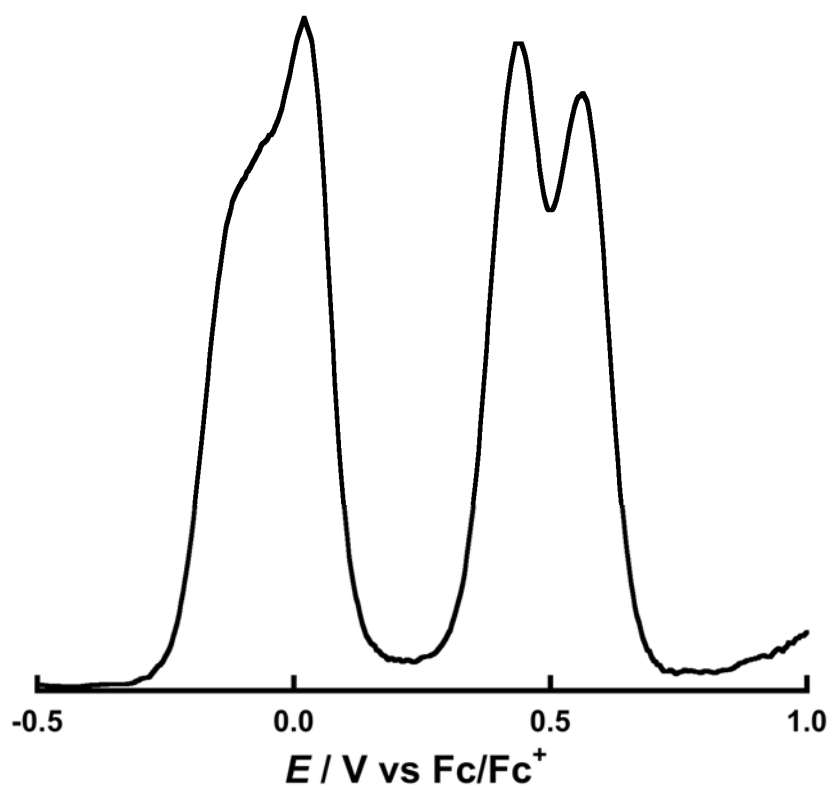


Fig. S1. Differential pulse voltammogram of **1** measured in CH_2Cl_2 containing 0.1 M $n\text{-Bu}_4\text{NBF}_4$ at 298 K (scan rate 0.1 V s^{-1}).

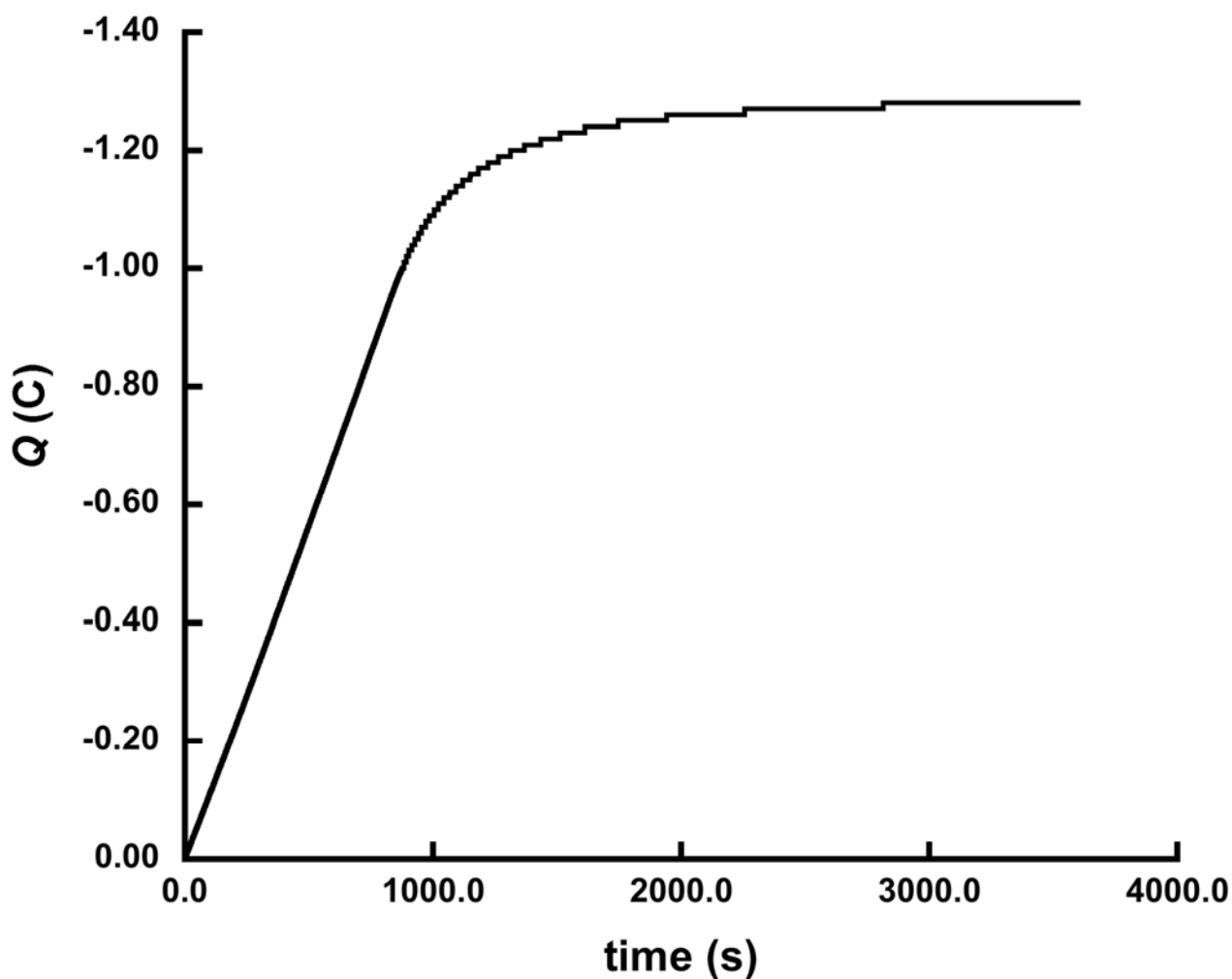


Fig. S2. Controlled potential coulometry at 0.2 V vs Fc/Fc^+ for **1** ($3.5 \mu\text{mol}$) in CH_2Cl_2 containing 0.1 M $n\text{-Bu}_4\text{NBF}_4$ at 298 K. The net charge Q was determined to be 1.26 C. Hence, 3.73 electrons (vertically four electrons) per molecule were removed at this potential. 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].

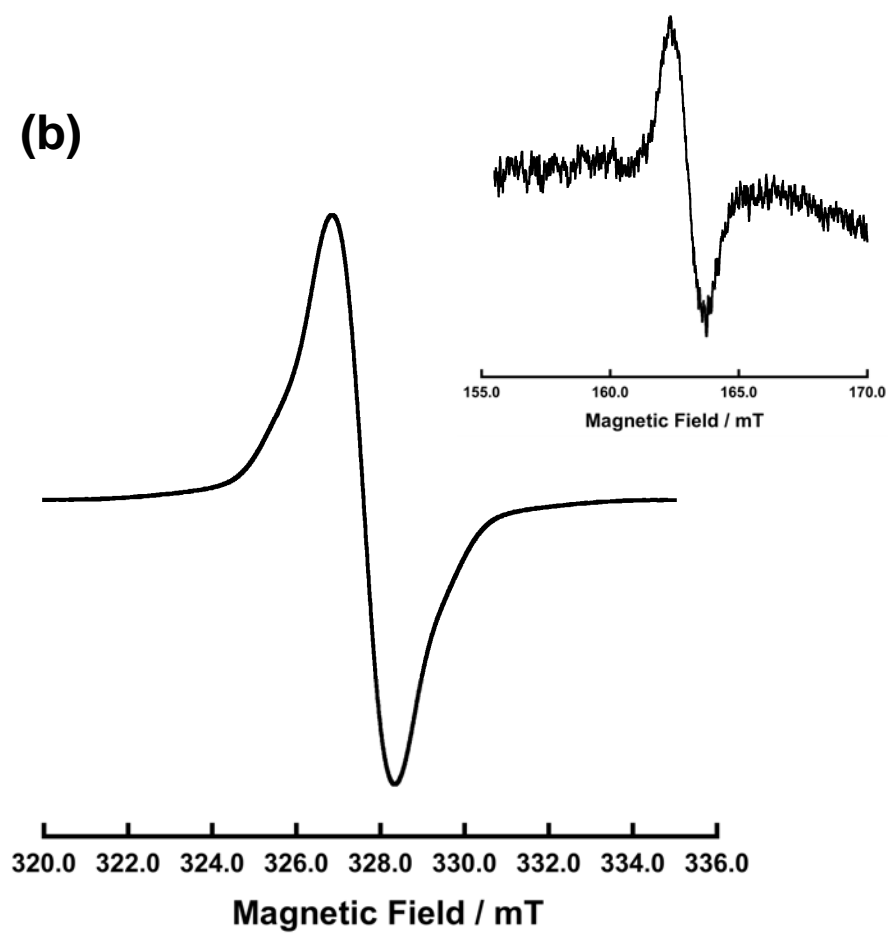
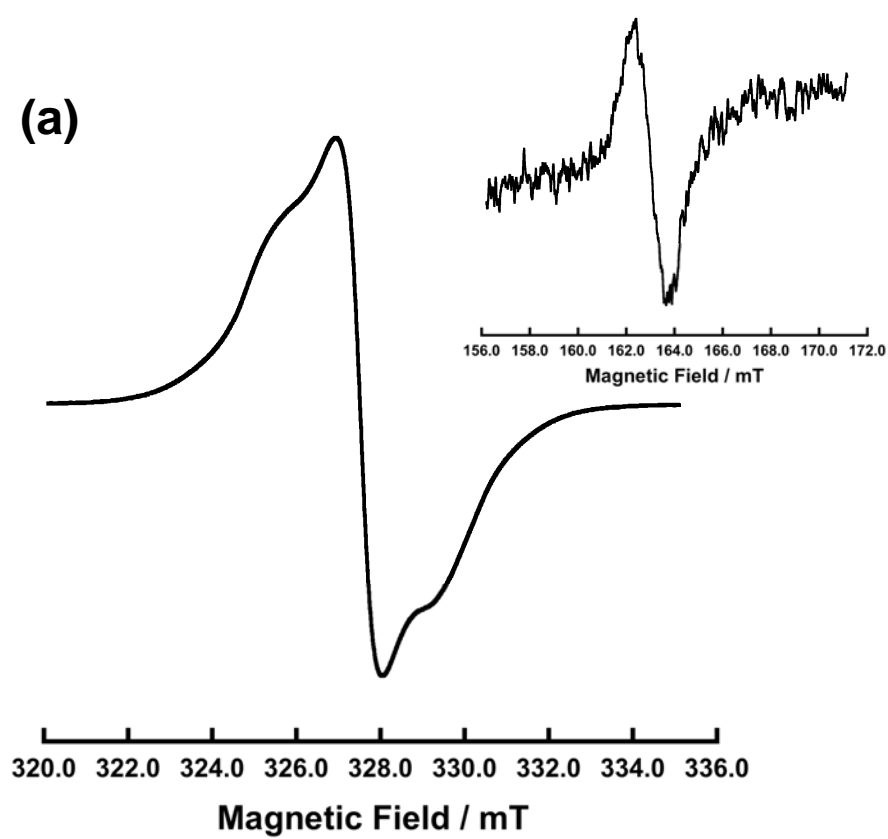


Fig. S3. CW-ESR spectra of **1** at 123 K after addition of (a) 2 equiv and (b) 4 equiv of oxidant.

Pulsed ESR Measurements: The magnetic moments with distinct spin quantum numbers (S) precess with their specific nutation frequency (ω_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 $\omega_n = [S(S+1) - M_S(M_S+1)]^{1/2} \omega_0$ under certain conditions. This indicates that ω_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 $S=1, 2$ and $\sqrt{6}$ for $S=2$. 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.

