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Macrocycles

1,3,5-Benzenetriamine Double- and Triple-Decker Molecules

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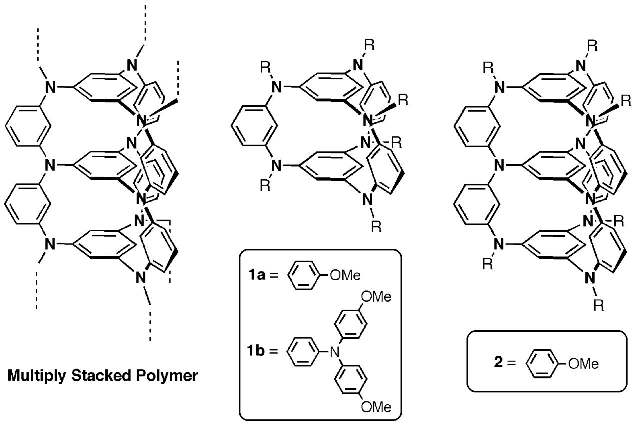
Triarylamine-based macromolecular systems are widely accepted as an appropriate electroactive material for the study of electronic, magnetic, and optical properties, and in fact oligoarylamines have been utilized as excellent hole-transport materials in photoconductors, light-emitting devices, and so forth.[1] This is mainly due to four factors: 1) low oxidation potentials; 2) stability of generated radical cations; 3) relatively small inner reorganization energy;[2] and 4) advances in palladium-catalyzed amination reactions,[3] which make it possible to synthesize structurally rigid and two-dimensionally expanded polymacrocyclic oligoarylamines.[4,5]

One-dimensional polyarylamines and their oligomers with *meta*-phenylene-linkage and/or alternating *meta*,*para*-phenylene-linkage in the polymer backbones can be considered as promising candidates for high-spin polymers.[6] However, in spite of various studies on polymers and/or oligomer model compounds, the generated spins in the oxidized state have been unfortunately shown to be mainly uncoupled except for the existence of minor high-spin components,[7] probably because of unexpected defects owing to insufficient oxidation and also interruption of π conjugation between spin-containing and ferromagnetic coupling units owing to undefined conformations of the one-dimensional polymer chain hamper the robust ferromagnetic exchange coupling pathway through the polymer backbone. Contrary to polyarylamines with one-dimensional connectivity, the retention of high-spin alignment has been accomplished for oligoarylamines incorporating rigid macrocyclic architectures.[5,8]

Inspired by the extensive work on multilayered cyclophanes from Misumi's group,[9] cylindrical cage-structured polyarylamines with increased connectivity among macrocycles (Scheme 1) are potentially intriguing to prevent the above-mentioned obstacles.[10] The hypothetical polymer shown in Scheme 1 can be regarded as a 1,3,5-benzenetriamine multiple-decker linked by three *meta*-phenylenes, or in other words, a cofacially stacked benzenes connected by three poly(*m*-aniline) strands. Herein we report the synthesis and characterization of the first double- and triple-decker arylamines **1** and **2** corresponding to dimeric and trimeric model compounds.[11] Compounds **1a** and **2** have anisyl groups at all *N*-positions to lower the oxidation potentials, and moreover, in **1b**, dianisylaminophenyl groups are attached at all *N*-positions to stabilize the oxidized state.[12]



Scheme 1. A hypothetical multiply stacked poly(arylamine) and 1,3,5-benzenetriamine double- and triple-deckers **1a**, **1b**, and **2** as oligomer model compounds.

1,3,5-benzenetriamine double- and triple-decker **1** and **2** were successfully obtained by repeatedly using Buchwald–Hartwig cross-coupling reaction[3] (Scheme 2).[13] In the synthesis of **1a** (and **1b**), the substituted benzenetriamines **3** (or **7**) and the corresponding tribromides **4** (and **8**) were coupled in a one-pot manner to make the cylindrical cage structure. On the other hand, the triple-decker compound **2** was prepared by the cross-coupling reaction between a dendritic oligoarylamine with six preorganized reaction points (**11**) and two equivalent of 1,3,5-tribromobenzene.

Colorless blocklike (**1a**) and platelike (**2**) single crystals were grown by slow evaporation of a dilute mixed solution (CH_3OH/CH_2Cl_2 for **1a**; THF/*n*-hexane for **2**) and their molecular structures were unequivocally determined by X-ray crystallography (Figure 1; Supporting Information, Table S1).[20] As shown in Figure 1a, **1a** adopts a C_3-symmetrical double-decker structure, where the two benzene rings as the decks were cofacially separated by 4.77 Å, and the dihedral angles between the cofacial 1,3,5-benzenetriamine planes and pillar-like three *meta*-phenylene planes were around 76–80°, thus demonstrating that the two cofacial benzene moieties

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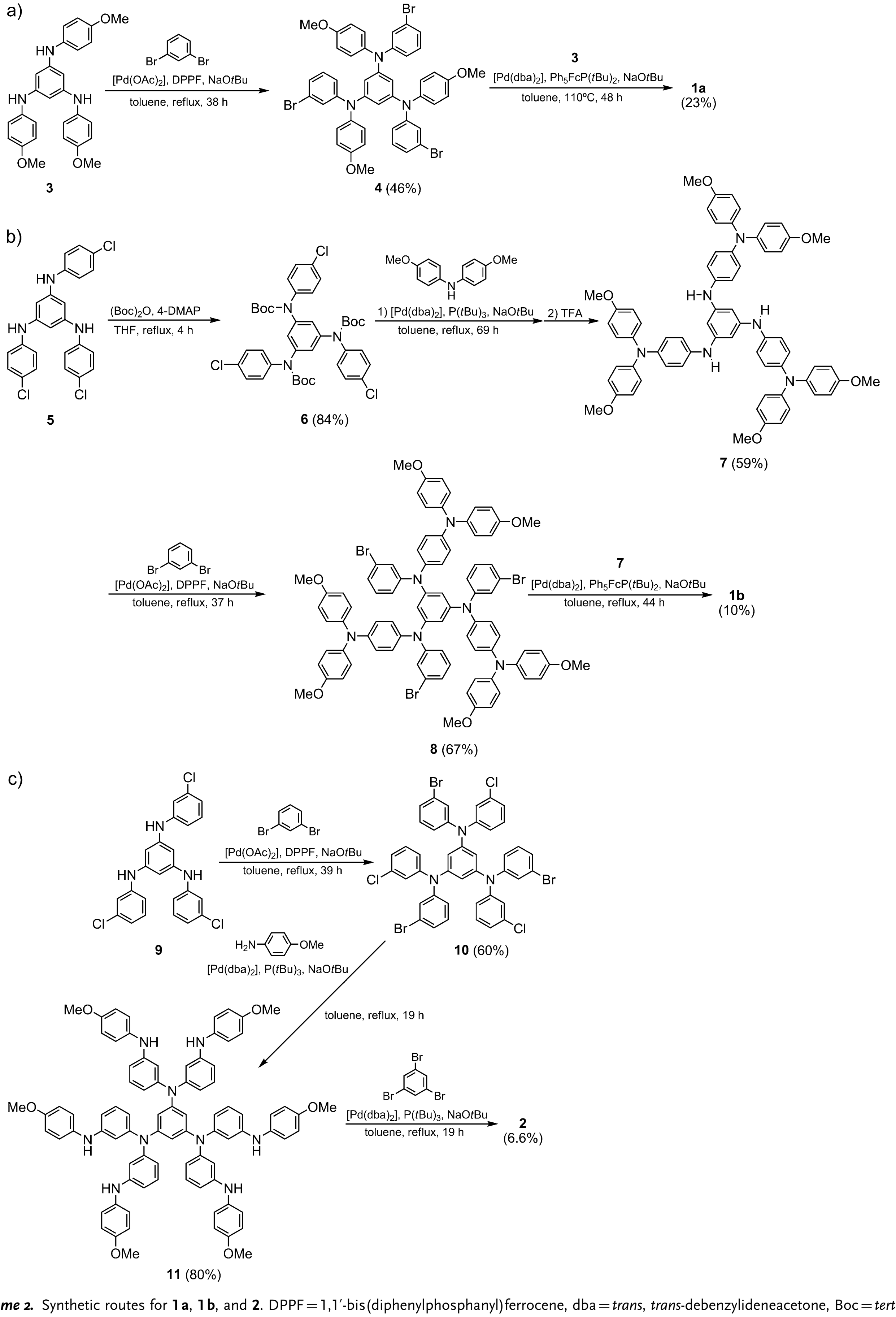

Scheme 2. Synthetic routes for **1a**, **1b**, and **2**. DPPF = 1,1′-bis(diphenylphosphanyl)ferrocene, dba = *trans*, *trans*-debenzylideneacetone, Boc = *tert*-butoxycarbonyl, 4-DMAP = 4-dimethylaminopyridine, TFA = trifluoroacetic acid.

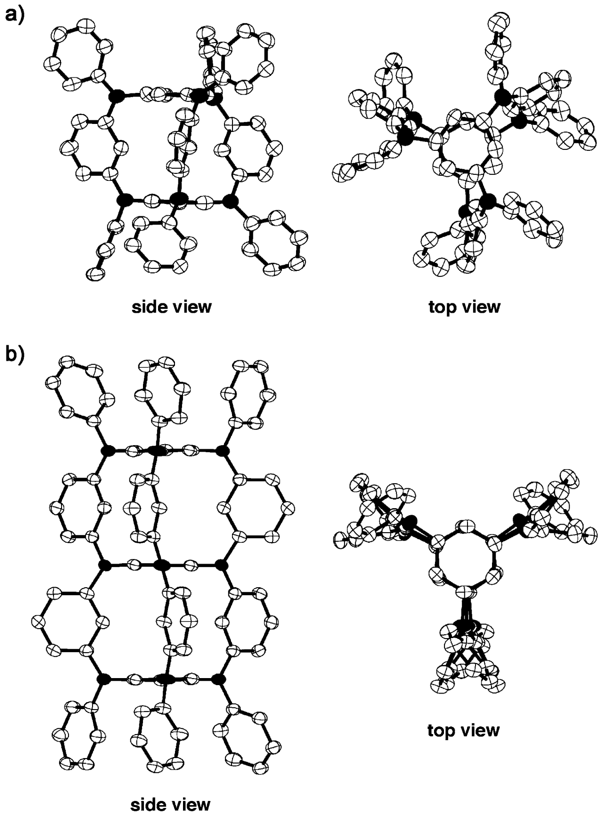

Figure 1. ORTEP representations of a) **1a** and b) **2**. Ellipsoids are set at 50% probability. Crystallization solvent molecules, methoxy groups, and hydrogen atoms are omitted for clarity. Nitrogen atoms are colored in black.

were not totally eclipsed but slightly twisted with each other (ca. 30°). On the other hand, although **2** also has a C_3-symmetrical triple-decker structure, distances between the cofacial benzene rings were estimated to be slightly longer than that of **1a** (4.84 Å), and moreover, the *meta*-phenylene pillars were nearly perpendicular to the 1,3,5-benzenetriamine planes. As a consequence, the three cofacial benzene moieties were confirmed to be nearly eclipsed with each other (Figure 1b).

To gain insight into the electronic structures of **1a** and **2**, we carried out density functional theory (DFT) calculations (at the B3LYP/6-31G* level) on the model molecules **1a**′ and **2**′[14] in which all the methoxy groups are omitted. The optimized structures were in good agreement with the X-ray structures. The frontier MOs comprised of HOMO and (HO-1)MO (Supporting Information, Figure S1) were virtually triply degenerate for **1a**′ (and quasi triply degenerate for **2**′). Moreover, those frontier MOs for **1a**′ and **2**′ were found to be distributed mainly over the three *meta*-phenylenediamine linkers, and therefore, the present double- and triple-decker molecules can be viewed as three oligo(*meta*-aniline) moieties that are linked by 1,3,5-benzentriyl decks (Supporting Information, Figure S1).

The redox behavior of **1a** and **2** was measured by cyclic voltammetry (CV) in CH_2Cl_2 (0.1M tetra-*n*-butylammonium tetrafluoroborate (nBu$_4$NBF$_4$)) at room temperature. Upon multisweep oxidation, both the peak current and the peak potential increased with repetitive potential cycling for **1a** and **2** (Supporting Information, Figure S2). This clearly indicates the electrochemical polymerization on the electrode surface owing to the instability of the oxidized species, though the detailed mechanism remains unclear. After 10 cycles, two discrete oxidation waves were observed at approximately 0.35 and 0.67 V vs. $Fc^{0/+}$ for the triple-decker species **2**, while single oxidation wave observed at 0.67 V vs. $Fc^{0/+}$ for double-decker compound **1a**. In contrast, the introduction of dianisylaminophenyl groups at all the *N*-positions of **1a** resulted in the recovery of reversible multiredox behavior, which is probably due to the existence of six *para*-phenylene diamine (PD) moieties as redox centers. As shown in Figure 2, the redox behavior of **1b** can be roughly estimated to be comprised of first two-electron, second four-electron, and third six-electron transfer processes, which means that double-decker **1b** is oxidizable up to a dodecacation. From the simulation of the observed differential pulse voltammogram (DPV),[15] the first and second oxidation processes of **1b** correspond to the generation of dication (quasi two-electron transfer: −0.12 (1e) and −0.06 (1e)) and hexacation (quasi four-electron transfer: +0.03 (4e)), respectively, and the third oxidation process can be judged to be quasi six-electron transfer (+0.44 (1e), +0.49 (1e), +0.51 (1e), +0.56 (1e), +0.60 (1e), and +0.61 (1e)). Therefore, these findings suggest that the diradical dication and hexaradical hexacation of **1b** can be generated by using appropriate oxidizing agents.

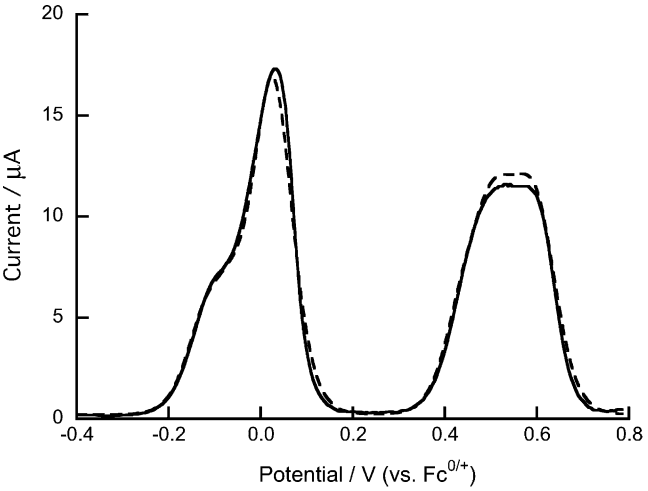

Figure 2. Differential pulse voltammogram (DPV) of **1b** in CH_2Cl_2 (0.1 M nBu$_4$NBF$_4$) measured with a Pt electrode (surface area 2 mm^2) at a sweep rate of 0.02 V s^{-1} at 298 K. The broken line indicates the simulated DPV (see text for details).

In conjunction with the fact that the same dianisylaminophenyl groups are substituted at all of the *N*-positions, the optical absorption spectroscopic changes of **1b** in CH_2Cl_2 during the course of the oxidation process were similar to those of the previously studied tetraaza[1$_4$]metacyclophane[12] (Figure 3). As shown in Figure 3a, a π–π* band with the λ_{max} of 333 nm in the neutral species **1b** was changed into three new bands corresponding to the oxidized species from **1b**$^+$ to **1b**$^{2+}$ (λ_{max} = 415, ca. 600, ca. 1000 nm) with an isosbestic point at 366 nm. The observed lowest energy band (λ_{max} ≈ 1000 nm) can be considered as the charge-resonance (CR) intervalence band (IV) band owing to the the semiquinone radical cation of the *para*-phenylenediamine (PD) moiety,[16] and slightly shifted hypsochromically with increasing oxidation number, whereas the next-lowest-energy band ($\lambda_{max} \approx 600$ nm) exhibited a slight bathochromic shift. Further oxidation of **1b**$^{2+}$ showed continuous increase in absorbance for the CR IV band, with a slight hypsochromic shift ($\lambda_{max} = 920$ nm), and the intensity reached up to thrice that of **1b**$^{2+}$, thus strongly indicating that **1b**$^{6+}$ was formed by oxidation of all the PD moieties of **1b** (Figure 3b). Note that the fact that the decrease in intensity observed in lower-energy region of the CR IV band with an isosbestic point at 1113 nm (Figure 3b, inset) on going from **1b**$^{2+}$ to **1b**$^{6+}$, demonstrates the existence of the charge transfer between the neutral and oxidized PD moieties through the *meta*-phenylene and 1,3,5-benzenetriyl linkers, as have been often observed in the mixed valence compounds with *meta*-phenylene and/or 1,3,5-benzenetriyl coupling units.[16c,17] Finally, the intense CR IV band decreased rapidly when **1b**$^{6+}$ is further oxidized, and two new bands with the λ_{max} of 524 and 723 nm grew with some isosbestic points (345, 450, and 796 nm), corresponding to a conversion from the semiquinoidal PD to the quinoidal PD (Figure 3c).

The reversibility of the multistage oxidation processes prompted us to determine the spin multiplicity of the polycationic species of **1b**. We have measured the electron spin transient nutation (ESTN) spectra based on the pulsed ESR spectroscopy[18] for the oxidized samples in a rigid glass of CH_2Cl_2 at 5 K. The stepwise chemical oxidation were carried out by adding 2 and 6 molar equivalents of tris(4-bromophenyl)aminium hexachloroantimonate (Magic Blue)[19] at 195 K. As shown in Figure 4a and Table 1, the

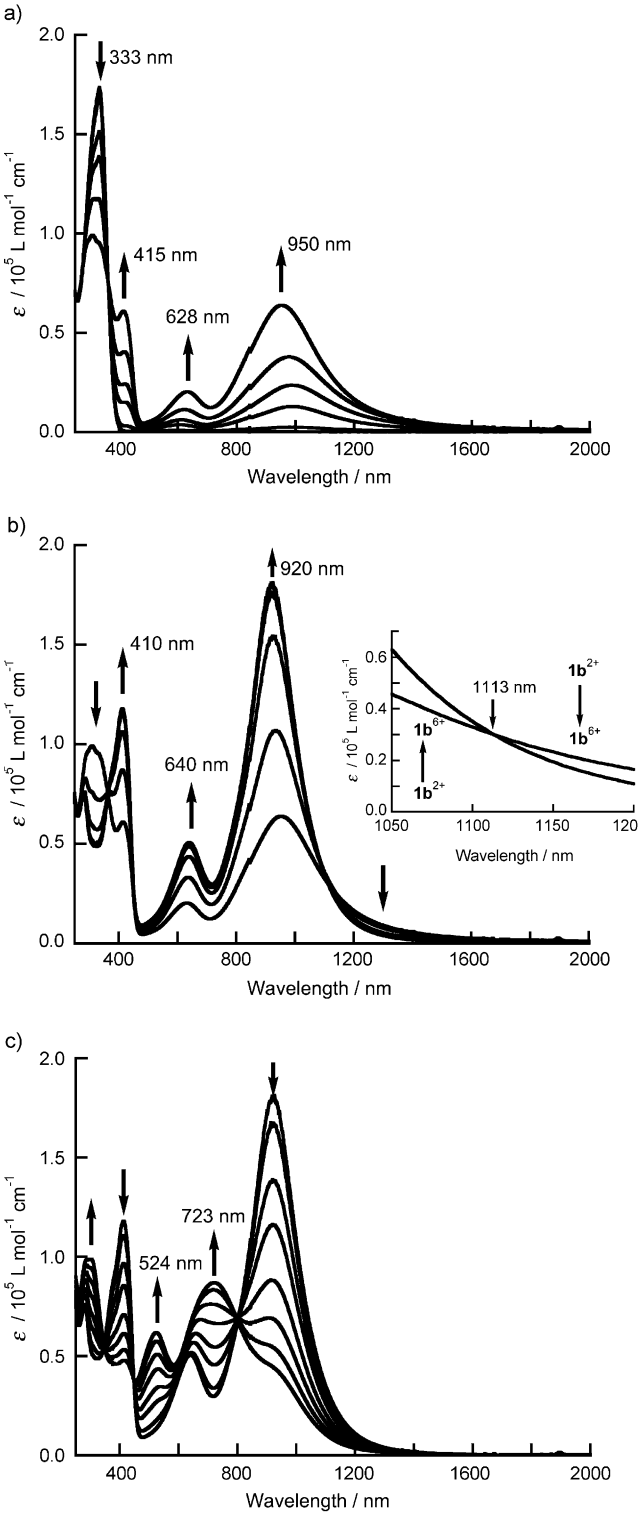

Figure 3. UV/Vis-NIR absorption spectra of the stepwise electrochemical oxidation of **1b** in CH_2Cl_2 (0.1 M/nBu$_4$NBF$_4$) at 298 K: a) **1b** to **1b**$^{2+}$; b) **1b**$^{2+}$ to **1b**$^{6+}$; c) further oxidation process from **1b**$^{6+}$.

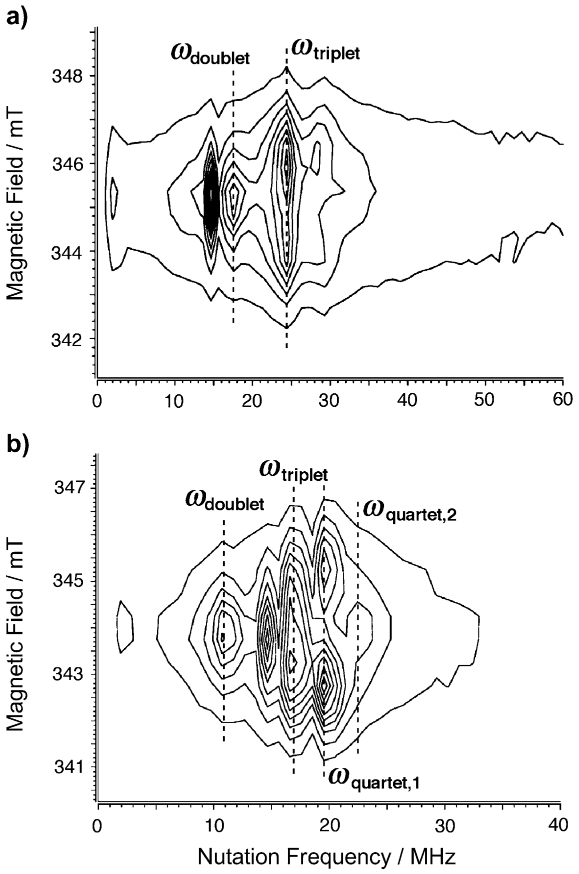

Figure 4. 2D ESTN spectra of **1b** in CH_2Cl_2 at 5 K after the addition of a) 2 equiv and b) 6 equiv of oxidant.

Table 1: Spectroscopic data of the ESTN spectroscopy for **1b**$^{2+}$ and **1b**$^{6+}$.

Species	Observed nutation frequency [MHz][a]	Transition assignment
1b^{2+}	24.4 ($\omega_t = \sqrt{2}\omega_d$)	$\lvert 1, \pm 1\rangle \Leftrightarrow \lvert 1, 0\rangle$
(doublet impurity)	17.8 (ω_d)	$\lvert 1/2, +1/2\rangle \Leftrightarrow \lvert 1/2, -1/2\rangle)$
1b^{6+}	19.5 ($\omega_{q,1} = \sqrt{3}\omega_d$)	$\lvert 3/2, \pm 3/2\rangle \Leftrightarrow \lvert 3/2, \pm 1/2\rangle$
	22.6 ($\omega_{q,2} = 2\omega_d$)	$\lvert 3/2, +1/2\rangle \Leftrightarrow \lvert 3/2, -1/2\rangle$
(triplet impurity)	16.6 ($\omega_t = \sqrt{2}\omega_d$)	$\lvert 1, \pm 1\rangle \Leftrightarrow \lvert 1, 0\rangle$
(doublet impurity)	11.0 (ω_d)	$\lvert 1/2, +1/2\rangle \Leftrightarrow \lvert 1/2, -1/2\rangle$

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

nutation frequency of 24.4 MHz observed after addition of 2 molar equiv of oxidant can be assigned to the spin-triplet state of **1b**$^{2+}$, judging from the nutation frequency owing to the spin-doublet impurity. This result is in good accordance with the DFT results that two electrons are removed from the degenerate HOMOs (Supporting Information, Figure S1). On the other hand, after oxidation of **1b** with 6 molar equiv of oxidant, two kinds of new signals at 19.5 and 22.6 MHz were detected along with those for the impurities with the spin-doublet (11.0 MHz) and spin-triplet (16.6 MHz) multiplicities (Figure 4b), and consequently, these nutation signals were assignable to the spin-allowed transition for the spin-quartet state from the frequency ratio. Therefore, this result suggests that **1b** treated with 6 equiv of oxidant is in spin-quartet state. However, the electronic structure of this high-spin state remains obscure at the present stage, and further examination is needed for elucidation of electronic structure for hexacation of **1b**.

In summary, we have succeeded in the preparation and characterization of 1,3,5-benzenetriamine double- and triple-decker compounds, which are the first examples of layered oligoarylamines stacked cofacially through multiple arene linkers. Furthermore, *N*-dianisylaminophenyl-group-substituted double-decker **1b** revealed reversible multiredox activity, and consequently, the polycationic species, which are generated by treatment of 2 and 6 equiv of oxidant, were found to be in high-spin state, as is reflected in the highly degenerate frontier MOs. Understanding the electronic structures of the polycationic species of the present compounds and the further attempts to create the related derivatives, which leads to the more robust high-spin polycationic species, which are currently being pursued in the context of exploitation of spin-polarized molecular wires.

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[13] Synthetic details for **1a**, **1b**, and **2** are described in the Supporting Information. As pointed out by one of the referees, an improvement in overall yields is needed for possible applications of these compounds.

[14] The full geometry optimizations of **1a′** and **2′** in C_3 symmetry were carried out by using Gaussian09 progaram package: Gaussian09 (Revision C.01), M. J. Frisch et al.

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[20] CCDC 879818 (**1a**) and CCDC 879819 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.