

# Trimacrocylic arylamine and its polycationic states†

Akihiro Ito,\*<sup>a</sup> Yuko Yamagishi,<sup>a</sup> Koji Fukui,<sup>a</sup> Syuuji Inoue,<sup>a</sup> Yasukazu Hirao,<sup>‡b</sup>  
Ko Furukawa,<sup>c</sup> Tatsuhi Kato<sup>d</sup> and Kazuyoshi Tanaka<sup>ab</sup>

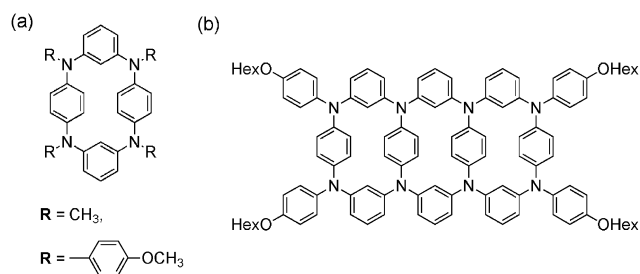
Received (in Cambridge, UK) 17th September 2008, Accepted 28th October 2008

First published as an Advance Article on the web 12th November 2008

DOI: 10.1039/b816311a

**A novel trimacrocylic arylamine was found to be accessible to the different spin-states by consecutive electrochemical or chemical oxidation.**

Alternating *meta*-phenylene- and *para*-phenylene-linked oligoaryl- amines are considered as promising molecular parts for the molecule-based electronics due to their intriguing magnetic and electronic properties.<sup>1–6</sup> From the magnetic view of point, the *meta*-phenylene linker plays a role in ensuring the effective ferromagnetic interaction, while the *para*-phenylene linker takes an important part in stabilizing the spin-containing aminium radical cations. Of the *meta*–*para*-oligoaryl amines prepared so far, the macrocyclic oligoaryl amines are structurally defined and, therefore, we can employ them as the component pieces to prepare the two- and/or three-dimensionally structured oligoaryl amines. The synthesis of tetraaza[14]*m,p,m,p*-cyclophane, the smallest macrocyclic oligoarylamine possessing the alternating *meta*–*para* linkage, has been reported independently at the same time by three groups (Fig. 1(a)).<sup>5</sup> Expectedly, these molecules were oxidized into di(radical cation) with parallel spin-alignment. Moreover, recently, Hartwig and co-workers have succeeded in synthesizing the three- and four-runged ladder-type oligoaryl amines (Fig. 1(b)).<sup>6</sup> However, the ground state of the dicationic species was determined to be a spin-singlet, although the generated spins are of delocalized character.



**Fig. 1** (a) Tetraaza[14]*m,p,m,p*-cyclophane and (b) its extension to the ladder-type trimacrocycle.

<sup>a</sup> Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, 615-8510 Kyoto, Japan. E-mail: aito@scl.kyoto-u.ac.jp

<sup>b</sup> CREST, Japan Science and Technology Agency (JST), Japan

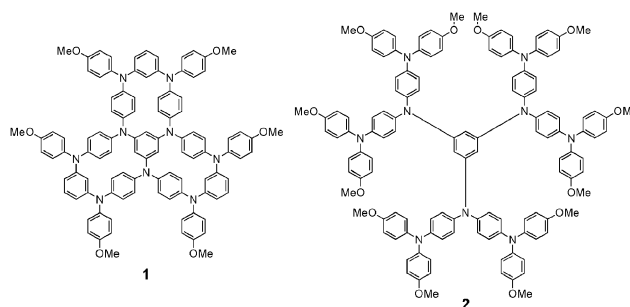
<sup>c</sup> Institute for Molecular Science, Myodaiji, 444-8585 Okazaki, Japan

<sup>d</sup> Department of Chemistry, Josai University, 1-1 Keyakidai, Sakado, 350-0295 Saitama, Japan

† Electronic supplementary information (ESI) available: Experimental section and the electrochemical and spectroscopic data. See DOI: 10.1039/b816311a

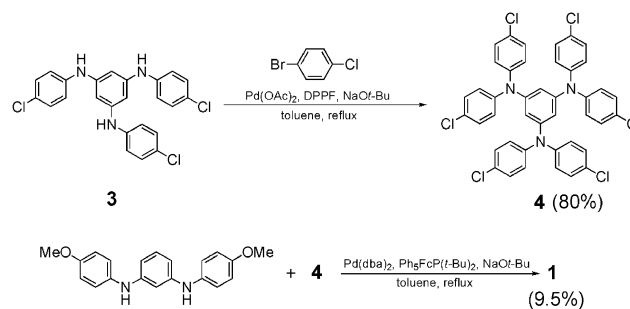
‡ Present address: Department of Chemistry, Graduate School of Science, Osaka University, 1-1 Machikaneyamacho, Toyonaka, Osaka 560-0043, Japan.

When the tetraazacyclophane structure in Fig. 1(a) is utilized as a building block for constructing the trimacrocylic oligoaryl- amine molecular system such as the ladder-type molecule in Fig. 1(b), there exists another option; the star-shaped extension. For the purpose of elucidating the electronic structures of polycationic species of the star-shaped trimacrocylic oligoaryl- amine, we synthesized a trimacrocycle **1**. The trimacrocycle **1** can also be regarded as an analog of the star-shaped oligoaryl- amine **2**. We have recently determined the spin multiplicities in tri(radical cation) of the star-shaped oligoarylamine **2**.<sup>3c</sup>



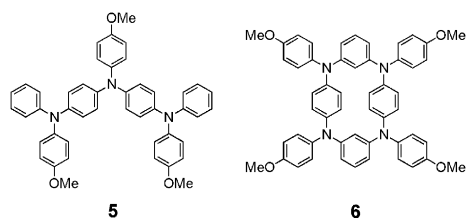
Palladium-catalyzed aryl amination reaction of 1,3,5-tris[di(4-chlorophenyl)amino]benzene (**4**) with 1,3-bis[(4-methoxyphenyl)amino]benzene gives the trimacrocycle **1** in around 10% yield, in a one-pot reaction (Scheme 1, ESI†).

Electrochemical oxidation of the trimacrocycle **1** by the cyclic voltammetry (CV) in CH<sub>2</sub>Cl<sub>2</sub> exhibits five redox couples as shown in Fig. 2. All the oxidation processes are chemically reversible after repeated potential cycling in CH<sub>2</sub>Cl<sub>2</sub>. Judging from the differential pulse voltammogram (Fig. S1, ESI†), the first four oxidations are regarded as one-electron transfer process, while the fifth oxidation corresponds to quasi-two-electron transfer, indicating **1** is oxidizable up to hexacation. The oxidation potentials of **1** are summarized in Table 1



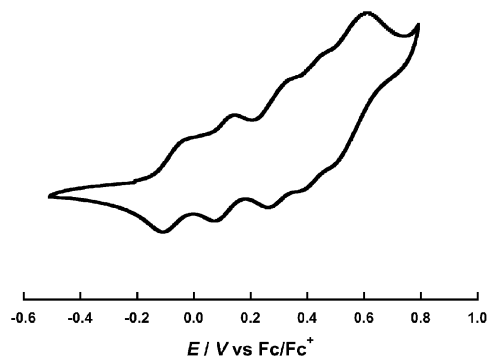
**Scheme 1** Synthesis of trimacrocylic arylamine **1**.

together with those of the related compounds under the same conditions.



From the comparison of the oxidation potentials for **1** with those for the star-shaped analog **2**, the first three oxidations are assigned as one-electron removal from each peripheral triamine moiety. Each oxidation potential of **1** shifts to the higher value as compared with the corresponding value of **2**. This situation closely relates to the fact that all the nitrogen atoms are inevitably charged after the three-electron removal from **1** and, therefore, the electrostatic repulsion on the peripheral *meta*-phenylenediamine moieties cannot be ignored, as shown in Fig. 3.

We measured the optical absorption spectral changes of **1** in CH<sub>2</sub>Cl<sub>2</sub> during the oxidation process of **1** to **1**<sup>3+</sup> by using an optically transparent thin-layer electrochemical cell. As shown in Fig. 4, the lowest-energy absorption band at λ<sub>max</sub> = 1336 nm grew together with the shoulder band at ~900 nm upon oxidation of **1** to **1**<sup>+</sup>. Further oxidation to the dication **1**<sup>2+</sup> resulted in a blue shift and increase in intensity of the lowest-energy band (λ<sub>max</sub> = 1154 nm). Finally, in the resulting trication **1**<sup>3+</sup>, further blue shift and increase in intensity of the lowest energy band (λ<sub>max</sub> = 1051 nm) were observed. Note that the similar spectral change was also seen during the oxidation process of **5** to **5**<sup>2+</sup> (Fig. S2, ESI<sup>†</sup>). The spectral

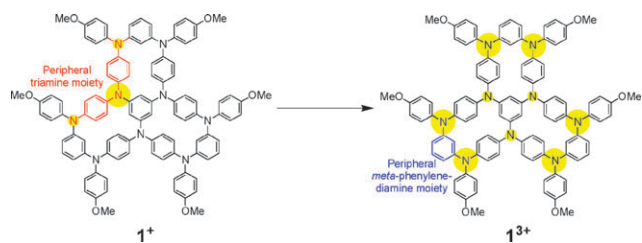


**Fig. 2** Cyclic voltammograms of **1** measured in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> at 298 K (scan rate 0.1 V s<sup>-1</sup>).

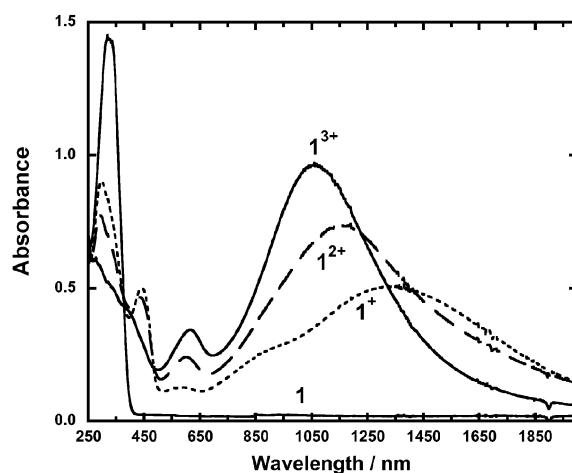
**Table 1** Oxidation potentials (in V) of **1** and the related compounds<sup>a</sup>

Compound	<i>E</i> <sub>1</sub>	<i>E</i> <sub>2</sub>	<i>E</i> <sub>3</sub>	<i>E</i> <sub>4</sub>	<i>E</i> <sub>5</sub>
<b>1</b>	-0.12	0.09	0.28	0.41	0.53 <sup>b</sup>
<b>2</b> <sup>c</sup>	-0.14	-0.01	0.09	0.19 <sup>d</sup>	—
<b>5</b>	-0.11	0.25	0.80 <sup>e</sup>	—	—
<b>6</b>	-0.01	0.22	0.54	0.67	—

<sup>a</sup> 1 mM CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub>, potentials vs. Fc/Fc<sup>+</sup>, Pt electrode, 298 K, scan rate 100 mV s<sup>-1</sup>. <sup>b</sup> Quasi-two-electron transfer. <sup>c</sup> Measured in PhCN (see ref. 3c). <sup>d</sup> Quasi-three electron transfer. <sup>e</sup> Anodic peak potential (irreversible).



**Fig. 3** Schematic view of the charge distribution (yellow circles) in the charged states **1**<sup>+</sup> and **1**<sup>3+</sup>.

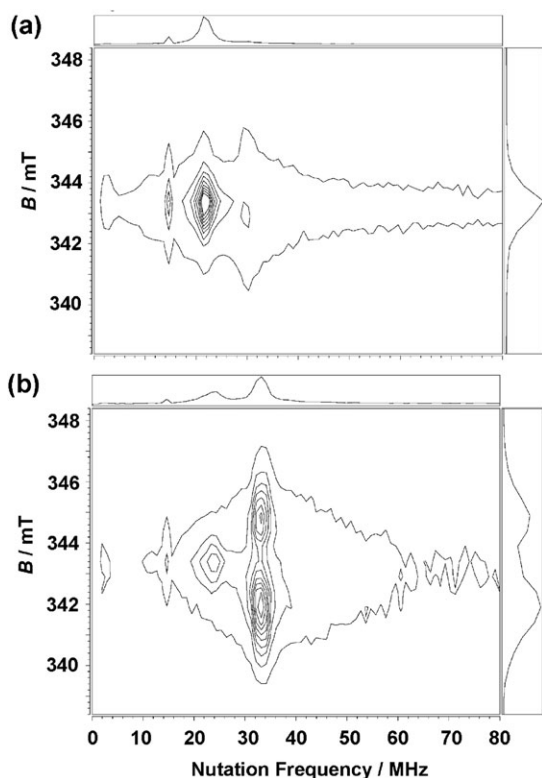


**Fig. 4** Vis-NIR spectra of the stepwise electrochemical oxidation of **1** to trication **1**<sup>3+</sup> in CH<sub>2</sub>Cl<sub>2</sub>/0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> at room temperature: (a) **1**<sup>+</sup> (dotted line), (b) **1**<sup>2+</sup> (broken line) and (c) **1**<sup>3+</sup> (solid line).

change in the charged states of **5** is expected to be influenced by the difference in charge distribution between **5**<sup>+</sup> and **5**<sup>2+</sup>; the generated charge in **5**<sup>+</sup> is considered to be distributed over the central triphenylamine moiety, whereas that in **5**<sup>2+</sup> is localized mainly on the outer two triphenylamine moieties to avoid the electrostatic repulsion. Therefore, it is anticipated that the charge distribution in the charged states of **1** changes from the central 1,3,5-triaminobenzene moiety to the peripheral three *meta*-phenylenediamine moieties, on going from **1**<sup>+</sup> to **1**<sup>3+</sup> (Fig. 3). This speculation can be supported by the comparison of the oxidation potentials for **1** with those for the triamine moiety **5** (Table 1). The first oxidation potentials of both **1** and **5** show almost the same value, while the third oxidation potential of **1** is similar to the second oxidation potential of **5**.

To explore the spin state of the each oxidized state of **1**, we measured the continuous wave ESR (cw-ESR) spectra of **1**<sup>+</sup>, **1**<sup>2+</sup>, **1**<sup>3+</sup> and **1**<sup>4+</sup> in a rigid-glass.<sup>7</sup> However, neither the definitive fine-structured spectra<sup>8</sup> nor the forbidden resonance<sup>8</sup> due to the existence of high-spin species were observed at 123 K (Fig. S3, ESI<sup>†</sup>).<sup>7</sup>

To overcome the difficulty in identifying the spin multiplicity of the high-spin components, we carried out the electron spin transient nutation (ESTN) measurements<sup>9</sup> based on the pulsed ESR method (Fig. 5 and S4, ESI<sup>†</sup>). As shown in Fig. S4a (ESI<sup>†</sup>), the nutation frequency (18 MHz = ω<sub>dication</sub> = ω<sub>doublet</sub>) observed at the central field is ascribed to |1/2, -1/2⟩ ↔ |1/2, +1/2⟩ transition of the spin-doublet **1**<sup>+</sup>. For the sample treated by 2 molar equiv. of oxidant, the new signal with the nutation



**Fig. 5** 2D ESR spectra of **1** in toluene/*n*-hexane at 5 K after the addition of (a) 2 equiv. and (b) 3 equiv. of oxidant.

frequency of 22 MHz ( $= \omega_{\text{dication}}$ ) appeared, and this corresponds to the  $|1, 0\rangle \leftrightarrow |1, \pm 1\rangle$  transition for the spin-triplet state (Fig. 5(a)). The generated triplet species can be regarded as  $\text{I}^{2+}$ . After oxidation of **1** with 3 molar equiv. of oxidant, two new intense signals with the same nutation frequency of 33 MHz ( $= \omega_{\text{trication}}$ ) were seen in addition to that for the spin-triplet species ( $\omega_{\text{dication}} = 24$  MHz) as impurities in the sample (Fig. 5(b)). From the frequency ratio ( $\omega_{\text{trication}}/\omega_{\text{doublet}} \sim \sqrt{3}$ ), these nutation signals are assigned to the  $|3/2, \pm 3/2\rangle \leftrightarrow |3/2, \pm 1/2\rangle$  transition for spin-quartet state, clearly indicating the dominance of spin-quartet  $\text{I}^{3+}$ . Finally, when 4 molar equiv. of oxidant is added, the observed nutation signals were detected at 25 MHz, corresponding to the generation of spin-triplet species on the basis of the frequency ratio ( $\omega_{\text{tetracation}}/\omega_{\text{doublet}} \sim \sqrt{2}$ ) (Fig. S4b, ESI<sup>†</sup>). Considering the quantity of added oxidant, the observed triplet species is considered as  $\text{I}^{4+}$ . This results suggests the newly generated spin is antiferromagnetically coupled to the existing three spins. As a whole, the consecutive oxidations of **1** lead to the charged states  $\text{I}^+$ ,  $\text{I}^{2+}$ ,  $\text{I}^{3+}$  and  $\text{I}^{4+}$  with doublet, triplet, quartet and triplet spin multiplicities, respectively, at low temperature.

In summary, we have prepared a novel trimacrocylic arylamine with a rigid molecular structure. From the electrochemical study, it was confirmed that this trimacrocycle is oxidizable up to the hexacation, and the chemically generated dication and trication are in high-spin triplet and quartet

states, respectively, whereas the tetracation is in low-spin triplet state probably because of the partial antiferromagnetic coupling among four radical spins. The present polymacrocylic molecular spin system may open the possibility for its extension to a larger two-dimensional molecular spin system.

The present work was supported by Grant-in-Aid for Scientific Research (B) (20350065) from the Japan Society for the Promotion of Science (JSPS) and from CREST (Core Research for Evolutional Science and Technology) of the Japan Science and Technology Agency (JST). Thanks are due to the Research Center for Molecular-Scale Nanoscience in the Institute for Molecular Science for the use of a pulsed ESR spectrometer.

## Notes and references

- (a) M. M. Wienk and R. A. J. Janssen, *Chem. Commun.*, 1996, 267; (b) M. M. Wienk and R. A. J. Janssen, *J. Am. Chem. Soc.*, 1996, **118**, 10626; (c) M. M. Wienk and R. A. J. Janssen, *J. Am. Chem. Soc.*, 1997, **119**, 4492; (d) M. P. Struijk and R. A. J. Janssen, *Synth. Met.*, 1999, **103**, 2287; (e) P. J. van Meurs and R. A. J. Janssen, *J. Org. Chem.*, 2000, **65**, 5712.
- (a) K. R. Sticley, T. D. Selby and S. C. Blackstock, *J. Org. Chem.*, 1997, **62**, 448; (b) T. D. Selby and S. C. Blackstock, *J. Am. Chem. Soc.*, 1998, **120**, 12155; (c) T. D. Selby and S. C. Blackstock, *J. Am. Chem. Soc.*, 1999, **121**, 7152; (d) T. D. Selby, K. R. Sticley and S. C. Blackstock, *Org. Lett.*, 2000, **2**, 171; (e) T. D. Selby, K.-Y. Kim and S. C. Blackstock, *Chem. Mater.*, 2002, **14**, 1685; (f) K.-Y. Kim, J. D. Hassenzahl, T. D. Selby, G. J. Szulczewski and S. C. Blackstock, *Chem. Mater.*, 2002, **14**, 1691; (g) J. C. Li, K.-Y. Kim, S. C. Blackstock and G. J. Szulczewski, *Chem. Mater.*, 2004, **16**, 4711.
- (a) A. Ito, A. Taniguchi, T. Yamabe and K. Tanaka, *Org. Lett.*, 1999, **1**, 741; (b) A. Ito, H. Ino, Y. Matsui, Y. Hirao and K. Tanaka, *J. Phys. Chem. A*, 2004, **108**, 5715; (c) Y. Hirao, H. Ino, A. Ito, K. Tanaka and T. Kato, *J. Phys. Chem. A*, 2006, **110**, 4866; (d) Y. Hirao, A. Ito and K. Tanaka, *J. Phys. Chem. A*, 2007, **111**, 2951; (e) A. Ito, S. Inoue, Y. Hirao, K. Furukawa, T. Kato and K. Tanaka, *Chem. Commun.*, 2008, 3242.
- (a) I. Kulszewicz-Bajer, M. Zagórska, I. Wielgus, M. Pawłowski, J. Gosk and A. Twardowski, *J. Phys. Chem. B*, 2007, **111**, 34; (b) I. Kulszewicz-Bajer, J. Gosk, M. Pawłowski, S. Gambarelli, D. Djurado and A. Twardowski, *J. Phys. Chem. B*, 2007, **111**, 9421; (c) M. Gałęcka, I. Wielgus, M. Zagórska, M. Pawłowski and I. Kulszewicz-Bajer, *Macromolecules*, 2007, **40**, 4924.
- (a) A. Ito, Y. Ono and K. Tanaka, *Angew. Chem., Int. Ed.*, 2000, **39**, 1072; (b) T. D. Selby and S. C. Blackstock, *Org. Lett.*, 1999, **1**, 2053; (c) S. I. Hauck, K. V. Lakshmi and J. F. Hartwig, *Org. Lett.*, 1999, **1**, 2057.
- X. Z. Yan, J. Pawlas, T. Goodson, III and J. F. Hartwig, *J. Am. Chem. Soc.*, 2005, **127**, 9105.
- The stepwise chemical oxidation with tris(4-bromophenyl)ammonium hexachloroantimonate (TBA·SbCl<sub>6</sub>) at 195 K in toluene/*n*-butyronitrile (8 : 2 (v/v)) generated the corresponding radical cations  $\text{I}^+$  to  $\text{I}^{4+}$ . Trimacrocycle **1** does not easily dissolve in polar solvents such as CH<sub>2</sub>Cl<sub>2</sub>, *n*-butyronitrile, and so forth, and thus, the measurements were executed only by using a dilute solution of toluene/*n*-butyronitrile. Therefore, we could not observe the forbidden  $\Delta M_S = \pm 2$  resonance in a half-field region of the allowed  $\Delta M_S = \pm 1$  resonance.
- W. Weltner, Jr, *Magnetic Atoms and Molecules*, Dover, New York, 1989.
- (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.