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Amine-based organic high-spin systems; a room-temperature-stable one-dimensional oligoaryl triamine-based tricationl

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ABSTRACT

A triamine, 2,2′,4,4′-tetrabromo-3″,4″-dimethyl-5,5′-bis(di(4-methylphenyl)amino)triphenylamine, was designed and synthesized as a model precursor for purely organic cationic high-spin systems. Cyclic voltammetry measurements revealed that the triamine gives stable mono-, di-, and tricationic states at ambient temperature. Novel electron transfer stopped-flow (ETSF) methods were invoked for characterizing the absorption spectra of the corresponding mono- and oligo-cationic states. The triamine-based trication was generated by chemical oxidation at room temperature, and the triamine was quantitatively recovered upon reduction. The electronic ground state of the trication is discussed.

1. Introduction

Recently, *meta*-connected oligoarylamines have attracted much attention as model precursors for positively charged organic high-spin systems [1,2]. As plural electrons are required to be removed from neutral precursors in solution to give the corresponding high-spin states, the occurrence of the stable oxidized oligo-cationic states in solution are of crucial importance. Thus, some structural modifications are necessary in order to improve the stabilities of the oxidized states: particularly the stabilization enables us to make various physicochemical measurements. When our research started a decade ago, the short-term goal was the detection of stable ground-triplet dications generated from oligoarylamines in solution. Monomeric triarylamines with various substituents at their *para* positions have been widely known to give extremely stable monocation radicals upon chemical or electrochemical oxidation [3]. Until now, extensive studies have been done on the design and synthesis of neutral oligoarylamine precursors by using these types of triarylamines as spin bearing units [2]. However, as previously pointed out by Stickley et al. [2f], the stability of monomeric cation radicals is not always a sufficient indicator of the stability of the corresponding oligo-cationic states of extended oligoarylamines. A relationship between the structures of oligoarylamines and the stabilities of their corresponding oligo-cations has been the focus of the current issues to establish molecular design rules for extended oligoarylamine-based high-spin systems.

Previously, we reported that oligo triarylamines with two or three *meta*-connected diarylamino groups (**1**, **2**) (Fig. 1) give stable di- and trications upon multi-electron oxidation, respectively [2b,c]. A novel electron spin transient nutation (ESTN) method was applied to the di- and trication, unequivocally identifying the spin multiplicities in their triplet and quartet ground state, respectively. In the designed molecules, four or six methoxy groups, i.e., strong electrodonating groups, are introduced to stabilize the di- or tricationic states, respectively. We have examined the relationship for a number of 1,3- bis(diarylamino)benzenes as exemplified by **1**, aiming to establish the molecular design rules to obtain diamine-based stable triplet dications in the ground state. Thus, an elaborate molecular design for tricationic entities has been challenging issues for us. Although we reported that a two-dimensionally extended triamine gives the corresponding stable trication in solution at low temperature [2b], 3,3′-bis(diarylamino)triphenylamines, as one-dimensionally extended triamines, emerge, which allow us to modify molecular structures easily in terms of synthetic chemistry. Recently, Ito et al. have reported a highly brominated derivative **3** (Fig. 2), which gives the corresponding stable dication upon two electrons oxidation [2g]. However, they failed to detect the corresponding trication with polybromo substitutions. Their results encouraged us to design and synthesize compound **4**, which has five electrodonating methyl groups at the peripheral rings and four bromo groups at the central rings. Compound **4** is expected to yield more thermodynamically stable mono- and oligo-cations than those of **3** [2i]. The CV measurements of **4** showed the generation of both stable dication $\mathbf{4}^{2+}$ and moderately stable trication $\mathbf{4}^{3+}$ at ambient

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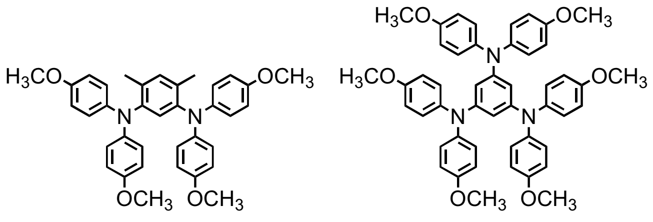


1 **2**

Fig. 1. Structures of *N,N,N′,N′*-tetrakis(4-anisyl)-4,6-dimethyl-1,3-phenylene-diamine (**1**) and *N,N,N′,N′, N″,N″*-hexakis(4-anisyl)-1,3,5-phenylenetriamine (**2**).

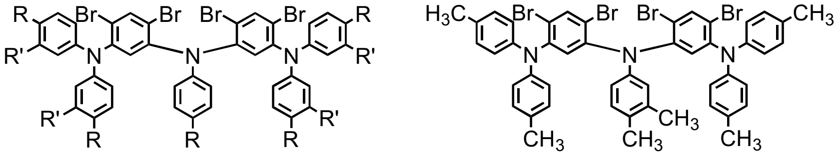
temperature. The electron transfer stopped-flow (ETSF) method allowed us to study the spectroscopic properties of the mono-, di- and tricationic states of **4**. These results are the first report on the detection of a one-dimensional oligoarylamine-based tricationic state [2j]. The enhancement of the thermodynamic and kinetic stability for oligo-cations of **4** is ascribed to the steric as well as electronic effects of the electrodonating methyl groups, which raise the HOMO energy level. The ESR study of the dication $\mathbf{4}^{2+}$ showed that the ground state is spin-triplet. The trication $\mathbf{4}^{3+}$ was not stable enough in a time scale for the conventional ESR sampling, indicating that chemical modification was not sufficient enough to stabilize the tricationic states in solution. We have also examined a highly alkylated triamine (**5**) with nine methyl groups at the peripheral aromatic rings, which gave stable mono- and dicationic state [2k]. Surprisingly, the peak of the trication $\mathbf{5}^{3+}$ completely disappeared in less than 0.2 s, indicating very unstable nature of the trication. The observations suggested that the introduction of extra methyl groups into the *meta* positions of the peripheral rings results in an unexpectedly large destabilizing effect on the tricationic states. An ESR study of the chemically oxidized **5** showed that the dication $\mathbf{5}^{2+}$ is spin-triplet in the ground state.

In this study, we have re-designed and synthesized a new alkylated triamine (**6**) with six methyl groups. The stabilities of the corresponding oligo-cationic states have been examined by using the cyclic voltammetry and ETSF method. The electronic states of the oligo-cationic states have been identified by cw-ESR measurements in rigid glass at low temperature.

2. Results and discussion

*2.2. Synthesis of 2,2′,4,4′-tetrabromo-3″,4″-dimethyl-5,5′-bis(di(4-methylphenyl)-amino)-triphenylamine (**6**)*

Compound **6** was synthesized and isolated as colorless powder by the similar method reported by Ito et al. [2g]. Dinitrotriarylamine (**7**) was reduced with SnCl$_2$/HCl to give diaminotriarylamine (**8**), which was reacted with 4-iodotoluene under Ullmann coupling condition to give a triamine (**9**). Compound **8** was brominated with benzyltrimethylammonium tribromide to give **6** in moderate yield (Fig. 3). All new compounds were fully characterized by spectroscopic methods. Data only for **6** and **9** are given below. Compound **9**: ^{1}H NMR (CDCl$_3$): δ 2.13 (s, 3H), 2.15 (s, 3H), 2.26 (s, 12H), 6.48–6.63 (m, 4H), 6.80 (t, 2H, $J = 3.2$ Hz), 6.87–7.05 (m, 21H), ^{13}C NMR (CDCl$_3$): 19.1, 19.9, 20.7, 116.9, 117.2, 118.4, 121.9, 123.8, 125.6, 129.3, 129.5, 130.2, 130.8, 131.7, 137.2, 145.0, 145.5, 148.3, 149.0. IR (KBr): 3019, 2916, 1570, 1508, 1292 cm^{-1}. M.p.: 84–85 °C.Compound **6**: ^{1}H NMR(CDCl$_3$): δ 2.08 (s, 3H), 2.15 (s, 3H), 2.26 (s, 12H), 6.46 (dd, 1H, $J = 8.0, 2.2$ Hz), 6.52 (d, 1H, $J = 2.2$ Hz), 6.62 (s, 2H), 6.72 (d, 8H, $J = 8.6$ Hz), 6.87 (d, 1H, $J = 8.6$ Hz), 6.97 (d, 8H, $J = 8.6$ Hz), 7.72 (s, 2H), ^{13}C



3: R=Br, R'=H
4: R=CH$_3$, R'=H
5: R=R'=CH$_3$

6

Fig. 2. Structures of 3,3′-bis(diarylamino)triphenylamines (**3**–**6**).

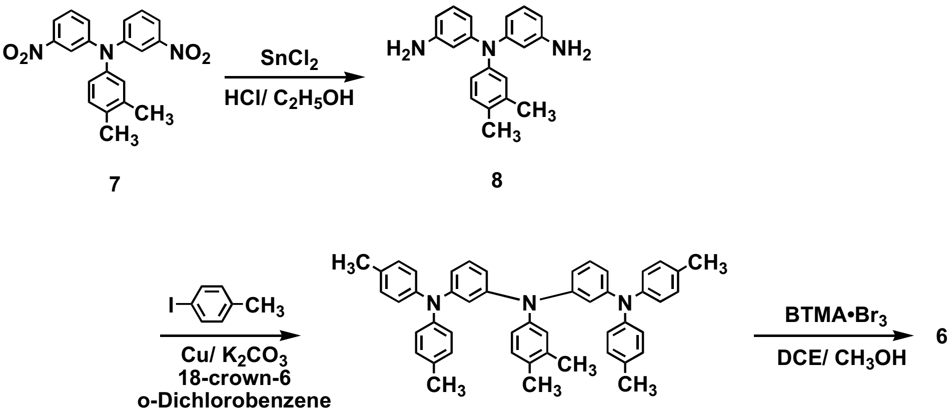


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Fig. 3. Synthetic route of **6**.