

# 2,6,10-Tris(dianisylaminium)-3,7,11-tris(hexyloxy)triphenylene: A Robust Quartet Molecule at Room Temperature

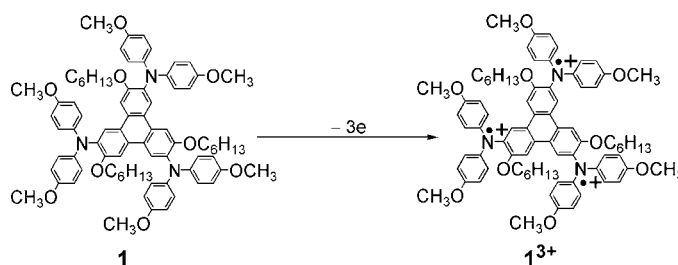
Eiji Fukuzaki and Hiroyuki Nishide\*

Department of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan

nishide@waseda.jp

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## ABSTRACT



A new triradical molecule, 2,6,10-tris(dianisylaminium)-3,7,11-tris(hexyloxy)triphenylene **1<sup>3+</sup>**, was synthesized by oxidative trimerization, palladium-catalyzed amination, and subsequent oxidation. It was chemically stable with a half-life > 1 month and displayed the magnetic parameter of  $S = 3/2$  even at room temperature.

There has been a continuous interest in the synthesis of high-spin organic molecules<sup>1</sup> because they are expected to be the spin module for forming a magnetically active bulk material. The high-spin behavior of molecules is derived from the spin alignment among the radicals' unpaired electrons conjugated with an aromatic pathway in a non-Kekulé and nondisjoint fashion (or a ferromagnetic connectivity).<sup>2</sup> The 1,3,5-substituted benzene core<sup>3,4</sup> and  $\pi$ -conjugated cyclic molecules, such as 2,8,14-benzenedehydro[12]annulene<sup>5</sup> and calix[4]arene-based polyradicals,<sup>6</sup> have been proposed and

synthesized as a ferromagnetic coupler for the multiradicals. However, these molecules have been obtained via tedious reaction steps and/or were difficult to utilize as a high-spin module for extending them to a high-spin polyradical or magnetically active and organic-based material.

Triphenylene<sup>7</sup> is known to have a cyclic and planar  $\pi$ -conjugated skeleton, and its derivatives have been extensively synthesized and studied as discotic liquid crystal molecules with functionalities, such as a photoconductive property.<sup>8,9</sup> For example, the columnar mesophase stack of hexapentyloxytriphenylene showed a charge migration with a significantly high mobility along the column.<sup>10</sup> In this study, we expected the triphenylene core to function as a new ferromagnetic coupler: through the planar and the cyclic

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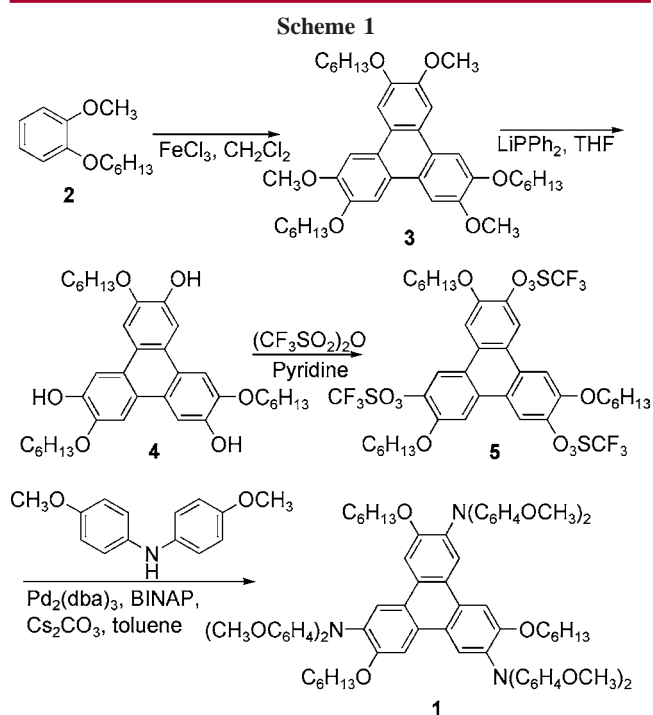
$\pi$ -conjugated skeleton of triphenylene, which has two rigid pathways for the interaction, the substituted three radicals' unpaired electrons could strongly interact and a spin defect which interrupts the interaction would not be vital, leading to a triplet molecule at room temperature.

Several groups reported the synthesis of symmetrical, unsymmetrical, and functionalized triphenylene derivatives. Some of the triphenylene derivatives are prepared by the trimerization of halogenated aryls using Pd coupling<sup>11</sup> and lithiation.<sup>12</sup> The unsymmetrical triphenylenes<sup>13</sup> are also synthesized by the coupling of the biphenyl precursor and the aryl substituted with different substituents. Among these synthetic routes of the triphenylene derivatives, the oxidative trimerization of phenyl ether<sup>14</sup> is one of the efficient routes to obtain a triphenylene with substituent groups on the 2, 6, and 10 positions, which possibly produce the ferromagnetic coupling.

For the molecular design of high-spin molecules, the second requisite is the selection of a stable organic radical species as the spin source. Molecules substituted with the triarylmethane radical and the phenoxy radical have been studied;<sup>15,16</sup> however, their high-spin states were observed only in a low-temperature range because of the chemical instability of these radical species. Chemically stable radical species are desired in such high-spin molecules to raise the temperature range of the spin alignment and possibly use them as a module for a molecular-based material. From among the list of radical species, the triarylammonium radical is a favorable candidate for the spin source which could fulfill the criteria of having both a substantial chemical stability even at room temperature and a strong spin polarization for spin alignment.<sup>16,17</sup> From such a viewpoint, a series of high-spin aminium radical modules have been synthesized;<sup>18</sup> however, they often lacked stability at room temperature and the quantitative radical (spin) generation because of their high oxidation potential and/or side reactions.

This paper describes a room-temperature robust quartet molecule, 2,6,10-tris(dianisylammonium)-3,7,11-tris(hexyloxy)-triphenylene **1**<sup>3+</sup>. We selected, for the first time, the 2,6,10-substituted triphenylene as a planar and  $\pi$ -conjugated ferromagnetic coupling core for the high-spin alignment. The 2,6,10-position of the triphenylene was very appropriate for significantly reducing both the steric hindrance of the radical moieties and electrostatic repulsion between the cationic radicals, which lead to the chemical stable molecule **1**<sup>3+</sup> with the spin alignment of  $S$  (spin quantum number) = 3/2.

The triphenylene core **3** was prepared by the oxidative trimerization of the 2-hexyloxyanisole **2** with FeCl<sub>3</sub> (Scheme 1).<sup>19</sup> The methoxy groups of **3** were converted to triflate



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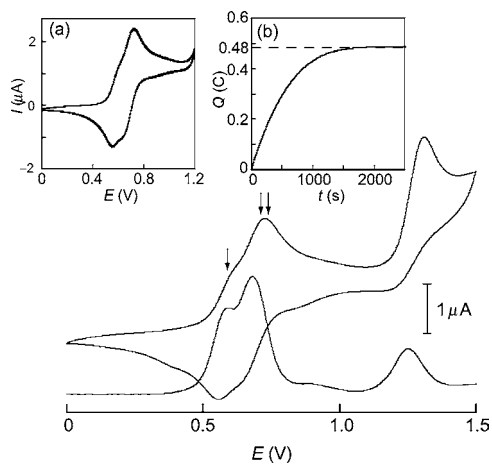
groups in compound **5** via selective ether cleavage and esterification. The 2,6,10-tris(*p*-dianisylamino)-3,7,11-tris-(hexyloxy)triphenylene **1** was obtained by Pd coupling of the triflates **5** with dianisylamine in the presence of Cs<sub>2</sub>CO<sub>3</sub>.<sup>20</sup> The yields of the trimerization and ether cleavage were 10 and 75%, respectively, which were comparable to those previously reported<sup>19</sup> for the corresponding reactions and fairly good for obtaining **1**. For the process from **5** to **1**, the triflate is a good leaving group to be substituted with the dianisylamine by the Pd coupling. **5** may be an effective intermediate to yield other radical (phenoxy, galvinoxyl, nitroxide, and nitronyl nitroxide) precursor-substituted triphenylenes. The NMR, IR, and mass spectra of **1** supported its structure. For example, two singlet signals of the protons and triplet signals of the hexyloxy groups on the triphenylene

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core were ascribed to the symmetrical structure of **1** and significantly shifted to a lower magnetic field (8.11, 7.61, and 3.89 ppm) due to the strong ring current effect of the triphenylene core in comparison with the protons on the diphenylamine groups.

Cyclic voltammetry of the triaminotriphenylene **1** showed characteristic redox waves. The first and second oxidation waves were chemically reversible (inset a of Figure 1). The

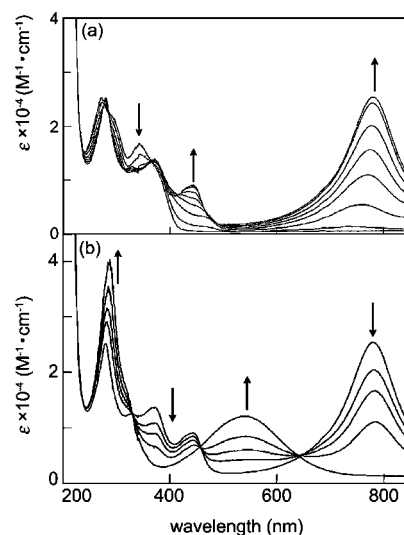


**Figure 1.** Cyclic and differential pulse voltammogram of **1** (0.33 mM) in  $\text{CH}_2\text{Cl}_2$  with 0.1 M  $(\text{C}_4\text{H}_9)_4\text{NBF}_4$  at room temperature and a  $50 \text{ mV s}^{-1}$  scan rate. Inset (a): repeatedly recorded voltammogram of **1** in the potential range of 0–1.0 V. Inset (b): controlled potential coulometry at 0.9 V for **1** ( $1.67 \times 10^{-6} \text{ mol}$ ) in  $\text{CH}_2\text{Cl}_2$  with 0.1 M  $(\text{C}_4\text{H}_9)_4\text{NBF}_4$  at room temperature. Potential vs Ag/AgCl.

voltammogram was repeatedly recorded 100 times for the potential (on 0–1.0 V) sweeps at room temperature. The redox potential was  $E^{\circ}(1) = 0.60$  and  $E^{\circ}(2) = 0.73$  V vs Ag/AgCl and ascribed to the one- and two-electron processes, respectively, also based on the differential pulse voltammetry of **1** (0.59 and 0.68 V, respectively). However, the third oxidation wave at  $E^{\circ}(3) = 1.30$  V (1.25 V in the differential pulse voltammetry) was irreversible, which was probably ascribed to overoxidation of the aminium cation or oxidation of the triphenylene core. Controlled potential coulometry was carried out on the **1** solution at 0.90 V (inset b of Figure 1), which quantitatively supported the triequivalent (three electrons) oxidation of **1** at the given potential.

The  $\text{CH}_2\text{Cl}_2$  solution of the triaminotriphenylene **1** was electrochemically oxidized at the applied potential of 0.9 or 1.5 V, and the reaction was monitored by in situ UV/vis and ESR spectroscopies. The UV/vis absorption ( $\lambda_{\text{max}} = 270, 343, \text{ nm}$ ) of the starting ESR-silent **1** decreased under the applied potential of 0.9 V, and new absorptions appeared at 442 and 782 nm with isobestic points at 276 and 365 nm (Figure 2a). These absorptions fairly agreed with those of a triarylaminium radical previously reported.<sup>21</sup> Upon the initial oxidation, the ESR showed a three-line absorption spectrum

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**Figure 2.** Electrolytic UV/vis spectrum of **1** (0.03 mM) in  $\text{CH}_2\text{Cl}_2$  with 0.1 M  $(\text{C}_4\text{H}_9)_4\text{NBF}_4$  at room temperature, at the given potential of 0.9 V (a) and oxidized at 1.5 V (b) vs Ag/AgCl.

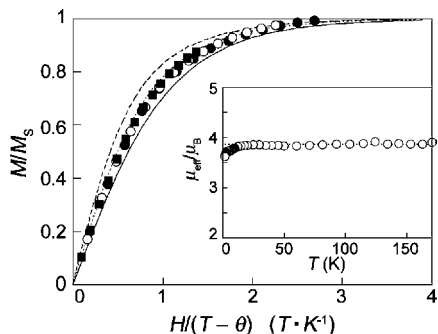
with  $g = 2.0031$ , indicating the generation of a nitrogen-centered radical. The ESR spectrum changed to a strong unimodal signal attributed to a high concentration with the applied time. These results indicated that the triaminotriphenylene **1** was oxidized to the aminium radical at 0.9 V, and the radical was chemically stable in  $\text{CH}_2\text{Cl}_2$  at room temperature.

On the other hand, the absorption spectrum of the aminium radical disappeared at the applied potential of 1.5 V, and a new absorption appeared at 540 nm with isobestic points at 329, 457, and 643 nm (Figure 2b). This spectrum resembled that of a dicationic phenylenediamine.<sup>21</sup> The ESR absorption completely disappeared at the applied potential of 1.5 V. These results suggested the overoxidation of  $\mathbf{1}^{3+}$  to an ESR-silent cationic state. These electrochemical measurements indicated that the triaminium triphenylene  $\mathbf{1}^{3+}$  was generated at the applied potential of 0.9 V vs Ag/AgCl.

On the basis of the electrochemical oxidation result,  $\text{AgBF}_4$  ( $E^{\circ} = 0.65$  vs ferrocene in  $\text{CH}_2\text{Cl}_2$ <sup>22</sup>) was selected as the oxidizing agent of **1** to yield  $\mathbf{1}^{3+}$ .  $\text{AgBF}_4$  is also characterized by its counteranion that possibly stabilizes the formed aminium cationic radical. The triaminotriphenylene **1** was treated with an equimolar amount of  $\text{AgBF}_4$  solubilized in the acidic mixture of trifluoroacetic acid, trifluoro anhydride, and  $\text{CH}_2\text{Cl}_2$  (vol 0.25/0.25/99.5). Upon oxidation, the solution turned a deep green, and the ESR spectrum gave a strong unimodal signal ( $g = 2.003$ ). The half-life of  $\mathbf{1}^{3+}$  was estimated by the ESR signal intensity to be 1.2 months at room temperature. The ESR at 100 K gave a quartet signal with a  $D$  value of  $0.0022 \text{ cm}^{-1}$ . The  $D$  value was compatible with that ( $0.0026 \text{ cm}^{-1}$ ) reported for the 1,3,5-benzene-based cationic triradical 1,3,5-tris(triphenylenediamino)benzene,<sup>17a</sup> which supported the formation of a N-centered and symmetrical triradical.

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The magnetization and static magnetic susceptibility of the triaminium triphenylene  $\mathbf{1}^{3+}$  in the frozen acidic  $\text{CH}_2\text{Cl}_2$  were measured by SQUID. The magnetization normalized with the saturated magnetization ( $M/M_s$ ) vs the ratio of magnetic field and temperature ( $H/(T - \theta)$ ) plots for  $\mathbf{1}^{3+}$  with a spin concentration (per the amine residue) of 0.9<sup>23</sup> were very close to the theoretical Brillouin curve for  $S = 3/2$ , indicating the quartet state of  $\mathbf{1}^{3+}$ . The ratio of the effective magnetic moment ( $\mu_{\text{eff}}$ ) and the Bohr magneton ( $\mu_B$ ),  $\mu_{\text{eff}}/\mu_B$ , vs temperature plots are shown in the inset of Figure 3. The  $\mu_{\text{eff}}/\mu_B$  values of  $\mathbf{1}^{3+}$  were almost constant in



**Figure 3.** Normalized plots of magnetization ( $M/M_s$ ) vs the ratio of the magnetic field and temperature ( $H/(T - \theta)$ ) for the triaminium triphenylene radical  $\mathbf{1}^{3+}$  with a spin concentration of 0.90 in  $\text{CF}_3\text{-COOH}/(\text{CF}_3\text{CO})_2\text{O}/\text{CH}_2\text{Cl}_2$  (0.25/0.25/99.5 vol %) at  $T = 2.5$  (●), 3 (○), and 5 (□) K and theoretical Brillouin curves corresponding to  $S = 2/2$ ,  $3/2$ , and  $4/2$ . Inset:  $\mu_{\text{eff}}/\mu_B$  vs  $T$  plots for  $\mathbf{1}^{3+}$  with a spin concentration of 0.90.

the range of 20–150 K<sup>24</sup> and agreed with the theoretical value of 3.87 for  $S = 3/2$ . These SQUID data indicated that the aminium triphenylene  $\mathbf{1}^{3+}$  is in a quartet ground state

with a very strong spin-exchange interaction between the unpaired electrons for  $\mathbf{1}^{3+}$ .

The magnetic susceptibility of  $\mathbf{1}^{3+}$  was also measured by the NMR shift method and the Evans equation<sup>25</sup> in the acidic  $\text{CD}_2\text{Cl}_2$  solution at high temperature. The susceptibility was estimated from the peak shift for a concentration series of the standard peak of cyclohexane in the deuterated  $\text{C}_6\text{D}_6$  solution. The  $\mu_{\text{eff}}/\mu_B$  value at 297 K was 3.78 (3.87 for the theoretical value of  $S = 3/2$ ) and was constant up to 333 K (60 °C).<sup>26</sup> These results revealed that a quartet state is stable even at room temperature.

In summary, three aminium radicals substituted on the 2,6-, 10-triphenylene in  $\mathbf{1}^{3+}$  were strongly coupled through the  $\pi$ -conjugated triphenylene core to be a quartet molecule even at room temperature. This quartet molecule is expected to be an effective module forming a high-spin polyradical and a high-spin liquid crystal.

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**Supporting Information Available:** Synthesis and characterization of the compounds, ESR spectra, and data of the NMR shift method. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(23) The spin concentration was determined by the saturated magnetization of the  $\mathbf{1}^{3+}$  sample.

(24) Above 180 K, the frozen medium was melted and the  $\mu_{\text{eff}}/\mu_B$  could not be determined because of the difficulty in the diamagnetic susceptibility correction.

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