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Triarylamines on [3]Radialene Scaffold: Novel [3]Radialene-based, Multistep, Wide-range Redox Systems with Remarkably Low Oxidation Potentials

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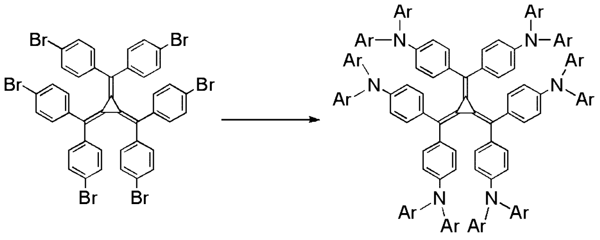
Hexakis[4-(diarylamino)phenyl][3]radialene derivatives show remarkably low oxidation potentials, suggesting the intramolecular through-space interaction between the facing triarylamine moieties. This through-space interaction is confirmed by the ESR spectrum of the corresponding oxidized species.

Owing to the unique structure and electronic properties, [3]radialene and its derivatives have received considerable attention from both theoretical and experimental points of view.[1,2] We previously reported the synthesis and physicochemical properties of a number of hexaaryl[3]radialene derivatives.[3] Among them, hexakis(4-bromophenyl)[3]radialene would be a versatile precursor for novel extended π systems having [3]radialene scaffold in view of the recent development of transition-metal-catalyzed cross-coupling reactions.[4] Now we focus on the [3]radialene derivatives **1a** and **1b** in which triarylamine moieties are incorporated into [3]radialene framework. Triarylamine moieties behave as electron donors and form triarylaminium radicals by chemical or electrochemical oxidation.[5] Combination of the π-electron system of [3]radialene with triarylamine moieties would give fascinating compounds with redox properties since hexaaryl[3]radialene derivatives behave as electron acceptors exhibiting two reversible reduction waves in relatively positive region. Another interest point is the possibility of the intramolecular through-space interaction between the facing triarylamine moieties or the corresponding aminium radicals. This interaction would be observed as the low oxidation potentials or the dipole–dipole interaction of the corresponding hexakis(cation radical). Here we report the synthesis and properties of **1a** and **1b**, [3]radialene-based fully-conjugated giant π-electron system, and their oxidized species.

The target [3]radialene derivatives **1a** and **1b** can be synthesized by the cross-coupling reaction of hexakis(4-bromophenyl)[3]radialene with the corresponding lithium diarylamide according to Hartwig's procedure (Scheme 1).[6] Under these conditions the [3]radialene framework remained intact. These new [3]radialene derivatives are stable, deep blue, crystalline compounds.[7]

These radialenes exhibit strong absorptions in the visible region at much longer wavelength (**1a**, 596 nm and **1b**, 603 nm in benzene)[8] than that of hexakis(4-bromophenyl)[3]radialene (485 nm). This red shift of the absorption is probably due to the intramolecular charge transfer by the incorporation of triarylamine moieties into electron-accepting [3]radialene framework. The FAB-MS spectra of **1a** and **1b** show the peaks corresponding to dication M^{2+} as well as the molecular ion peak,[8] suggesting the strong electron-donating properties. ^{1}H NMR spectrum of **1a** shows the inner phenyl protons (δ 6.61 and 6.84) at considerably higher field than those of outer tolyl protons (δ 6.98 and 7.04), suggesting an intramolecular stacking propeller conformation.



1a (Ar = *p*-tolyl)
1b (Ar = *p*-methoxyphenyl)

Scheme 1. Synthesis of the [3]radialene derivatives **1a** and **1b**. *Reagents and conditions*: Ar_2NLi (9.6 equiv), [Pd(P(*o*-tolyl)$_3$)$_2$] (4 mol %), P(*o*-tolyl)$_3$ (2 mol %), toluene, reflux, 4 h, 72% (**1a**), 55% (**1b**).

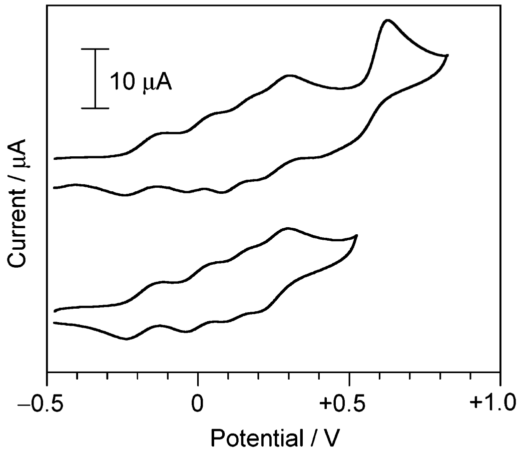


Figure 1. Cyclic voltammograms of **1b**.

By the measurement of cyclic voltammograms (CV) it is found that these [3]radialene derivatives serve as an amphoteric, multistep redox system (Figure 1). Both **1a** and **1b** exhibit four consecutive reversible oxidation waves followed by a fifth irreversible wave and two reduction waves (Table 1). It should be noted that even the third oxidation potentials of **1a** and **1b** are lower than the oxidation potentials of tris(*p*-tolyl)amine (+0.37 V) and tris(*p*-methoxyphenyl)amine (+0.15 V) under similar conditions. Three electron oxidation of **1** would give the corresponding tris(cation radical) $\mathbf{1}^{3+}$ where the radical centers are apart from each other and close to the facing triarylamino moiety. Therefore, the charge delocalization between the

Table 1. Redox potentials of **1a** and **1b**[a]

	$^5E_{ox}$[b]	$^4E_{ox}$	$^3E_{ox}$	$^2E_{ox}$	$^1E_{ox}$	$^1E_{red}$	$^2E_{red}$[b]
1a	+0.76	+0.31	+0.16	+0.04	−0.13	−1.89	−2.27
1b	+0.62	+0.24	+0.13	0.00	−0.18	−1.97	−2.42

[a]V vs. Fc^+/Fc, in CH_2Cl_2 (0.1 M n-Bu_4NClO_4), scan rate; 50 mV s^{-1}, 25 °C. [b]Peak potential.

aminium radical and the facing amino groups might play a crucial role for the remarkably low oxidation potentials. This intramolecular interaction would be clear if the dipole–dipole interaction is observed in the corresponding hexakis(cation radical) **1^{6+}**. Although the number of electrons involved in each oxidation wave is not clear from the CV, normal pulse voltammetry (NPV)[8] suggests that each of four reversible reduction waves involves one electron and that the fifth irreversible wave involves two electrons. The reversibility of the fourth oxidation wave indicates the stability of tetrakis(cation radical) **1^{4+}**, probably due to the conjugation between the triarylamine moieties through the [3]radialene core. The reduction potentials are also more negative than those of hexakis(4-bromophenyl)[3]radialene ($^1E_{red} = -1.55$ V, $^2E_{red} = -2.03$ V).

The treatment of **1b** with 3 equivalents of thianthrenium tetrafluroborate ($Th^+BF_4^-$)[9] in degassed acetonitrile–butyronitrile (1:1 v/v) at room temperature gives the corresponding tris(cation radical) **1b^{3+}** that is stable in degassed solution for several days. The solution is also deep blue exhibiting an absorption maximum ($\lambda_{max} = 730$ nm) at longer wavelength than **1b**. ESR spectrum in the frozen solution at 77 K exhibits only broad signal without any signals assignable to multiplet species to suggest that the average distance between the radical centers in **1b^{3+}** is too long to observe any fine structures. On the other hand, the treatment of **1b** with 6 equivalents of $Th^+BF_4^-$ give rise to a further oxidized species ($\lambda_{max} = 642$ nm) that shows typical ESR signals for triplet species (Figure 2). The zero-field splitting parameters are estimated to be $D = 14.0$ mT and $E = 0$ mT, and the distance between the radical centers by point-dipole approximation is calculated to be about 5.8 Å. This distance is consistent with the distance between the facing triarylaminium radicals with the consideration of the steric repulsion between the bulky triarylamino groups. Consequently, we conclude that this dipole–dipole interaction is attributable to the facing triarylaminium radicals. The triplet species should be a further oxidized species by more than three electrons. Further studies on these oxidized species, particularly on **1b^{6+}**, are now in progress.

In summary, we have synthesized novel [3]radialene derivatives **1a** and **1b** in which the electron-donating triarylamine moieties are incorporated into the electron-accepting [3]radialene framework. They exhibit remarkably low oxidation potetials owing to the through-space interaction between the facing triarylamine moieties. This through-space interaction is also confirmed by ESR spectra of the oxidized species of **1b**.

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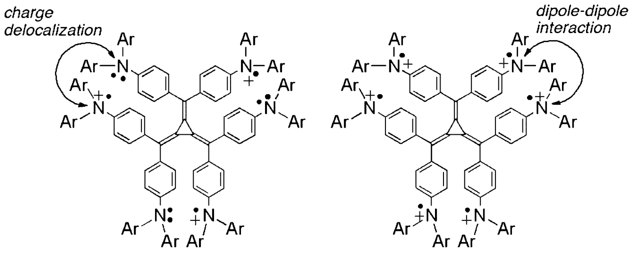

1^{3+} **1^{6+}**

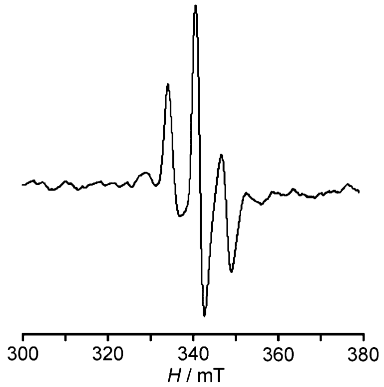

Figure 2. ESR spectrum of the mixture of **1b** and 6 equiv of $Th^+BF_4^-$ in acetonitrile–butyronitrile (1:1 v/v) at 77 K.

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7 Spectroscopic data for **1a**: deep blue crystals; mp 197–198 °C; MS (FAB): $m/z = 1706$ (M^+); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 36H), 6.61 (d, $J = 8.9$ Hz, 12H), 6.84 (d, $J = 8.9$ Hz, 12H), 6.98 (d, $J = 8.6$ Hz, 24H), 7.04 (d, $J = 8.6$ Hz, 24H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.81, 117.07, 119.19, 125.10, 128.10, 129.58, 131.07, 132.15, 134.39, 144.90, 146.62; UV–vis (benzene): λ_{max}/nm ($\log \varepsilon$) 316 (5.03), 472 (4.69), 596 (4.87); Anal. Calcd for $C_{126}H_{108}N_6$: C, 88.69; H, 6.38; N, 4.93%. Found: C, 88.43; H, 6.27; N, 4.90%. **1b**: deep blue crystals; mp 198–199 °C; MS (FAB): $m/z = 1898$ (M^+); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (s, 36H), 6.56 (d, $J = 8.5$ Hz, 12H), 6.76 (d, $J = 9.0$ Hz, 24H), 6.83 (d, $J = 8.0$ Hz, 12H), 7.10 (d, $J = 9.0$ Hz, 24H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.43, 114.64, 117.31, 118.07, 119.71, 126.90, 131.30, 134.12, 140.91, 147.21, 155.72; UV–vis (benzene): λ_{max}/nm ($\log \varepsilon$) 311 (5.02), 478 (4.60), 603 (4.81); Anal. Calcd for $C_{126}H_{108}N_6O_{12}$: C, 79.72; H, 5.73; N, 4.53%. Found: C, 79.39; H, 5.65; N, 4.34%.

8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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