# Synthesis of Nonaphenylenes and Dodecaphenylenes Using Electron-transfer Oxidation of Lipshutz Cuprate Intermediates

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Nonaphenylene and its hexaalkyl derivatives have been synthesized using electron-transfer oxidation of Lipshutz cuprates with duroquinone. Oxidation of the Lipshutz cuprate derived from dibromo-*o*-terphenyl in THF produced nonaphenylene in moderate yield, whereas the similar oxidation of the Lipshutz cuprate derived from diiododiethyl-*o*-terphenyl in ether afforded the corresponding nonaphenylene and dodecaphenylene. Furthermore, oxidation of Lipshutz cuprate derived from diiododibutyl-*o*-terphenyl only gave the nonaphenylene.

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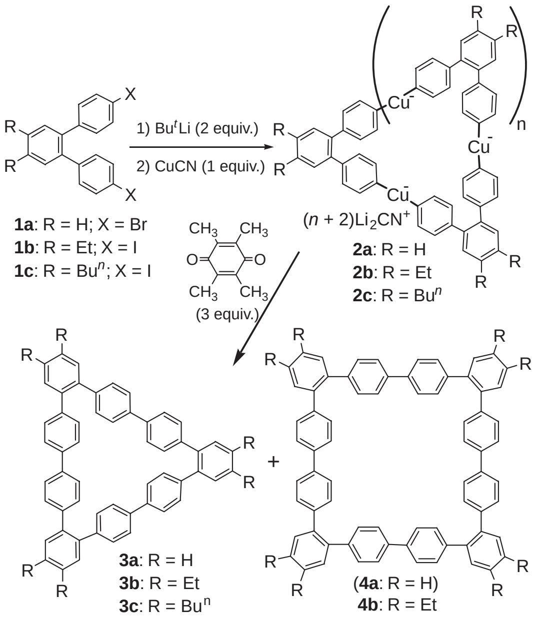
Cyclophanes and cyclic oligophenylenes have attracted considerable attention among experimental and theoretical chemists,[1,2] because these molecules exhibit unique structures, $\pi$–$\pi$ interaction, absorption and emission properties, and host ability in host–guest chemistry.[1a,3] Although nonaphenylene was first synthesized in 1969 using $CuCl_2$-mediated coupling of a di-Grignard derivative,[2b] its detailed properties have never been clarified presumably owing to its low yield. In the course of our research on aryl–aryl couplings,[4] we found a simple and convenient homo-coupling of aryl lithium via the electron-transfer oxidation of Lipshutz cuprates with duroquinone that produces biaryls in high yields.[5] Since this new coupling can be expected to have a wide applicability for the synthesis of large-membered oligophenylenes, we employed this procedure for the cyclo-oligomerization of **1** (Scheme 1).



**Scheme 1.** Synthesis of **3** and **4** using electron-transfer oxidation of **2a**–**2c**.

As shown in Scheme 1, the Lipshutz cuprates **2a**–**2c** were generated by the reaction of **1a**–**1c**[6] with 2 equiv. of *t*-BuLi, followed by treatment with 1 equiv. of CuCN in THF (for **1a**) or ether (for **1b** and **1c**) at −78 °C. For the coupling of the cuprate **2a**, oxidation of **2a** with 3 equiv. of duroquinone in THF at rt proceeded smoothly to afford nonaphenylene **3a** in 46% yield.[7] In the case of **2b**, all reactions can be carried out in ether owing to the higher solubility of **1b**, **2b**, and their related compounds. Thus, the coupling of **2b** with 3 equiv. of duroquinone in ether at −78 °C–rt produced **3b** (25%), together with **4b** (5%). In addition, the coupling of **2c** with duroquinone under the same conditions afforded only **3c** in 15% yield. Thus, the reactivity of **2b** and **2c** for the electron-transfer oxidation is different, although the selectivity for the cyclooligomerization is difficult to explain at this stage. Since only a limited number of reactions can be applied for the synthesis of cyclic oligophenylenes, electron-transfer oxidation of Lipshutz cuprates can be expected to be a powerful tool for the construction of macrocyclic oligophenylenes.

To determine the molecular structure of **3**, X-ray analysis of **3b** was carried out.[8] As shown in Figure 1, **3b** has a high crystallographic $D_3$ symmetry with a $C_2$ axis passing through the midpoint between C(1)–C(1)* and C3–C(3)* bonds. The molecular structure of **3b** is exactly triangular, and the corner three benzene rings and all C–C bonds between benzene rings are coplanar. The torsion angles of the *o*-terphenylene and biphenylene units are ca. 60° and ca. 50°, respectively, indicating a fairly twisted conformation of the biphenylene units.

The cyclic oligophenylenes **3a**–**3c** and **4b** exhibit strong fluorescence with high quantum yields. As shown in Figure 2, the

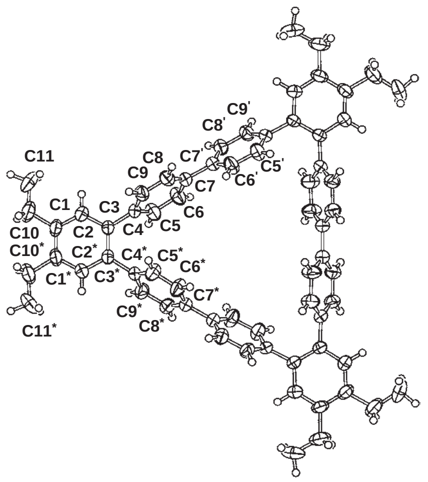


**Figure 1.** Crystal structure of **3b**. The selected bond lengths (Å) are as follows: C(1)–C(1)* 1.403(4), C(1)–C(2) 1.379(2), C(2)–C(3) 1.395(2), C(3)–C(3)* 1.398(3), C(3)–C(4) 1.495(2), C(4)–C(5) 1.378(2), C(5)–C(6) 1.387(2), C(7)–C(7)′ 1.485(3).

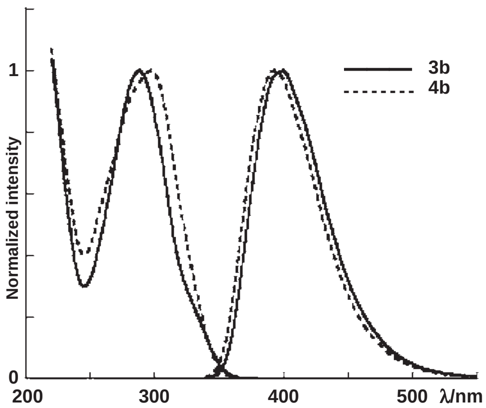


**Figure 2.** Normalized electronic and fluorescence spectra of solutions of **3b** and **4b** in THF.

electronic spectra of **3b** and **4b** show the longest absorption maxima at 288 ($\log \varepsilon = 5.01$) and 297 ($\log \varepsilon = 5.09$) nm, whereas the fluorescence spectra of **3b** and **4b** exhibit emission at 400 ($\Phi_F = 0.92$) and 393 ($\Phi_F = 0.91$) nm, respectively. Since **4b** has a larger $\pi$-system than **3b**, the absorption maximum of **4b** shifts to a longer wavelength than that of **3b**. In contrast, the emission of **3b** shifts to a longer wavelength than that of **4b**, presumably due to a slightly smaller HOMO–LUMO gap.[9]

The redox properties of **3b** and **4b** were investigated using cyclic voltammetric analysis. Interestingly, **3b** in 1,2-dichlorobenzene showed a reversible reduction ($E^{red}{}_{1/2} = -1.47$ V vs Fc/Fc$^+$) and an irreversible oxidation ($E^{ox} = 1.10$ V vs Fc/Fc$^+$). In a similar manner, **4b** showed a reversible reduction ($E^{red}{}_{1/2} = -1.45$ V vs Fc/Fc$^+$) but no oxidation was observed in the range of 0.5 to 1.5 V vs Fc/Fc$^+$. Thus, **3b** and **4b** seem to have similar HOMO and LUMO levels due to the similar arrangement of phenylene units. The results of the MO calculations for the HOMO and LUMO levels of **3b** and **4b** are consistent with the redox potentials of these compounds.[9]

The cyclic oligophenylenes **3a**–**3c** and **4b** form silver complexes with AgOTf, $AgClO_4$, and $AgOCOCF_3$ in $CD_2Cl_2$ and $CDCl_3$. Thus, the $^1$H NMR chemical shifts of the aromatic protons in **3a**–**3c** and **4b** are shifted downfield by 0.04–0.26 ppm, when **3a**–**3c** and **4b** are mixed with silver salts in $CD_2Cl_2$ and $CDCl_3$. According to the small association constants of the silver complex formation, the UV spectrum of **3c**•$AgClO_4$ in $CH_2Cl_2$ exhibits a small blue shift as compared to that of **3c** [**3c**: $\lambda_{max}$ 291 nm → **3c**•$AgClO_4$: $\lambda_{max}$ 287 nm]. Interestingly, the quantum yield of the emission (396 nm) of **3c**•$AgClO_4$ in $CH_2Cl_2$ decreased to $\Phi_F = 0.61$ as compared to the emission of **3c** at 397 nm ($\Phi_F = 1.00$).

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6 The starting materials **1b** and **1c** were prepared starting from 4,5-diethyl-1,2-diiodo- and 4,5-dibutyl-1,2-diiodobenzenes. The palladium-catalyzed cross-coupling of 4,5-diethyl-1,2-diiodo- and 4,5-dibutyl-1,2-diiodobenzenes with 4-trimethylsilylphenylzinc chloride, followed by the reaction with ICl afforded **1b** and **1c**, respectively.

7 Selected data **3b**: colorless cryst. mp 278–280 °C (decomp.), LDI-TOF MS ($m/z$) 852 (M$^+$); $^1$H NMR ($CDCl_3$) $\delta$ 7.49 (d, $J = 8.3$ Hz, 12H), 7.30 (s, 6H), 7.15 (d, $J = 8.3$ Hz, 12H), 2.76 (q, $J = 7.5$ Hz, 12H), 1.31 (t, $J = 7.5$ Hz, 18H); $^{13}$C NMR ($CDCl_3$) $\delta$ 140.9, 140.7, 138.2, 137.5, 130.2, 129.8, 125.6, 25.2, 15.2; UV (THF) $\lambda_{max}$ ($\log \varepsilon$) 288 (5.01), 325sh (4.48). **4b**: colorless cryst. mp 288–290 °C (decomp.), LDI-TOF MS ($m/z$) 1138 (M$^+$); $^1$H NMR ($CD_2Cl_2$) $\delta$ 7.36 (d, $J = 8.3$ Hz, 16H), 7.20 (s, 8H), 7.16 (d, $J = 8.3$ Hz, 16H), 2.67 (q, $J = 7.1$ Hz, 16H), 1.21 (t, $J = 7.1$ Hz, 24H); $^{13}$C NMR ($CDCl_3$) $\delta$ 141.1, 140.2, 138.9, 137.2, 130.7, 130.1, 126.5, 25.4, 15.4; UV (THF) $\lambda_{max}$ ($\log \varepsilon$) 297 (5.09). **3c**: colorless cryst. mp 254.5–255.5 °C, LDI-TOF MS ($m/z$) 1020 (M$^+$); $^1$H NMR ($CD_2Cl_2$) $\delta$ 7.48 (d, $J = 8.3$ Hz, 12H), 7.24 (s, 6H), 7.15 (d, $J = 8.3$ Hz, 12H), 2.71 (t, $J = 8.1$ Hz, 12H), 1.68–1.62 (m, 12H), 1.51–1.43 (m, 12H), 0.98 (t, $J = 7.3$ Hz, 18H); $^{13}$C NMR ($CD_2Cl_2$) $\delta$ 141.4, 140.4, 138.5, 137.9, 131.1, 130.6, 126.0, 34.1, 32.5, 23.3, 14.2; UV ($CH_2Cl_2$) $\lambda_{max}$ ($\log \varepsilon$) 288 (4.87), 323sh (4.41) nm.

8 X-ray data for **3b**: $C_{66}H_{60}$, $M_r$ 853.20, trigonal, $R\bar{3}c$ (No. 167), $Z = 6$, $a = 17.904(2)$ Å, $c = 28.214(4)$ Å, $V = 7832(1)$ Å$^3$, $D_{calcd} = 1.085$ g cm$^{-3}$, $T = 298$ K, $\mu$(Mo K$\alpha$) = 0.61 cm$^{-1}$, Rigaku AFC7R, Mo K$\alpha$ ($\lambda = 0.71069$ Å), 4277 reflections were collected, 3994 unique ($R_{int} = 0.059$), 1584 reflections used to calculate $R_1$, 101 parameters, $R_1 = 0.055$, $wR_2 = 0.175$, GOF = 1.19.

9 The calculated HOMO and LUMO levels (HF/6-31G*): **3a**, −7.516 and 2.684 eV; **4a**, −7.496 and 2.607 eV; the calculated HOMO and LUMO levels (PM3): **3a**, −8.814 and −0.379 eV; **4a**, −8.838 and −0.384 eV.

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