

Facile Synthesis and Lateral  $\pi$ -Expansion of Bisanthenes

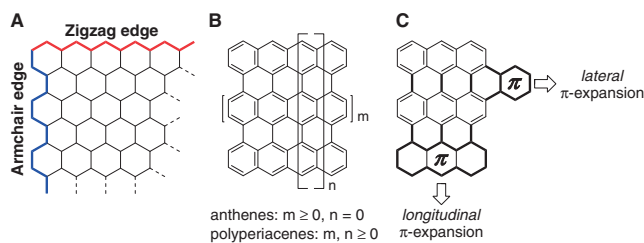
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The improved Scholl reaction allows for the direct cyclization of anthracene oligomers to give bisanthene, teranthene, and quateranthene. Furthermore, a variety of  $\pi$ -expanded bisanthenes are obtained by the Diels–Alder cycloaddition of bisanthene with several arynes. These reactions would allow us to synthesize various size- and shape-controlled polyperiacenes.

Polycyclic aromatic hydrocarbons (PAHs) have been regarded as suitable model compounds for elucidating the fundamental structure–property relationships of nanographenes and graphene nanoribbons (GNRs).<sup>1</sup> It is predicted that a localized nonbonding  $\pi$ -state is generated only around the zigzag edges, referred to as “edge state,”<sup>2</sup> while armchair edges do not have such a state. Anthenes<sup>3</sup> and polyperiacenes,<sup>4</sup> in which two or more anthracenes or acenes are condensed in the *peri*-directions, have been good candidates for small segments of GNRs, since they can have the well-defined two edge structures; zigzag and armchair edges (Chart 1). Recent theoretical and experimental studies reveal that anthenes and polyperiacenes can inherently possess the same electronic structure as the edge state of zigzag-edged GNRs (ZGNRs), which depends on the edge shape and the molecular size.<sup>3–5</sup> In this context, the organic synthesis of the well-terminated and size-controlled ZGNR molecules are in high demand,<sup>6</sup> not only because of the fundamental structure–property studies, but also because of the potential application of the magnetic and optical properties originating from the edge state to spintronics<sup>7</sup> and nonlinear optical devices.<sup>8</sup> Despite the best candidates of the ZGNRs segments, the reported anthenes and their derivatives, even bisanthene,<sup>9</sup> the smallest, are subjected to long multistep syntheses and poor total yields, which would hamper extensive studies of them. Of great importance is to develop a facile route toward precise  $\pi$ -expansions in the longitudinal and lateral directions (Chart 1C).

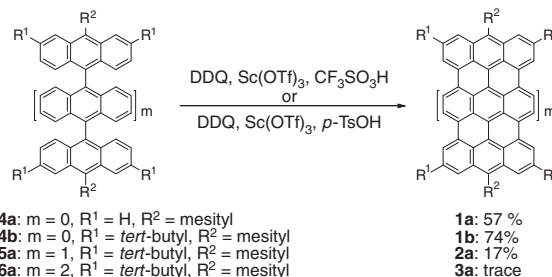
With this in mind, we report the facile synthesis and the lateral  $\pi$ -expansion of bisanthene. The former is the direct cyclization of the anthracene oligomer in the *peri*-direction by



**Chart 1.** (A) Edge structures of nanographene. (B) Molecular structures of anthenes and polyperiacenes. (C) Precise  $\pi$ -expansions.

using improved Scholl conditions, which is applicable to the synthesis of longer anthenes (teranthene and quateranthene), and the latter is the ring-condensation at the bay region of bisanthene by employing the cycloaddition with arynes.

The Scholl reaction, which involves the oxidative dehydrocyclization of aromatic compounds, would be a most promising synthetic method for our purpose of the direct cyclization of anthracene oligomers (Scheme 1).<sup>10</sup> The reaction conditions of the synthesis of bisanthene derivatives from the corresponding bianthryls are summarized in Table 1.<sup>11</sup> Dehydrocyclization of bianthryl **4a** under the conventional Scholl conditions using oxidants, such as  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ , and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)/acid,<sup>13</sup> gave only a trace amount of **1a** or uncharacterized complex mixtures (Entries 1, 2, and 5), presumably due to the steric hindrance of the precursors and to the instability of bisanthenes under harsh conditions. However, treatment of **4a** or **4b** with excess DDQ– $\text{Sc}(\text{OTf})_3$  in the presence of trifluoromethanesulfonic acid or *p*-toluenesulfonic acid (*p*-TsOH) furnished the corresponding bisanthenes **1a**<sup>14</sup> and **1b**<sup>14</sup> in good yields (Entries 6 and 7). Because the reaction using DDQ in the absence of Brønsted or Lewis acids results in quantitative recovery of the precursor (Entries 3–5), it can be



**Scheme 1.** Direct syntheses for anthenes under the improved Scholl conditions.

**Table 1.** Reaction conditions for the synthesis of bisanthenes **1a** and **1b**

Entry	Starting material	Conditions			Yield/%	
		Oxidant	Lewis acid	Brønsted acid	<b>4</b>	<b>1</b>
1	<b>4a</b>	$\text{AlCl}_3$	—	—	—	trace
2	<b>4a</b>	$\text{FeCl}_3$	—	—	—	Complex mixture
3	<b>4a</b>	DDQ	—	—	>99	—
4	<b>4a</b>	DDQ	$\text{Sc}(\text{OTf})_3$	—	>99	—
5	<b>4a</b>	DDQ	—	<i>p</i> -TsOH	>99	—
6	<b>4a</b>	DDQ	$\text{Sc}(\text{OTf})_3$	$\text{CF}_3\text{SO}_3\text{H}$	—	42
7	<b>4a</b>	DDQ	$\text{Sc}(\text{OTf})_3$	<i>p</i> -TsOH	—	57
8	<b>4a</b>	DDQ	$\text{Bi}(\text{OTf})_3$	<i>p</i> -TsOH	>99	—
9	<b>4b</b>	DDQ	$\text{Sc}(\text{OTf})_3$	$\text{CF}_3\text{SO}_3\text{H}$	—	21
10	<b>4b</b>	DDQ	$\text{Sc}(\text{OTf})_3$	<i>p</i> -TsOH	—	74

concluded that the combination of all three components plays a main role in forming the bisanthenes. Although the mechanistic details of the reaction have not been clarified yet, strong Brønsted acids may promote protonation of the anthracene ring and electron transfer to DDQ, and arenium-type cations may be generated as intermediate species.<sup>13,15,16</sup> In comparison with the previous synthetic methods of the *meso*-substituted bisanthenes reported by Maulding,<sup>17a</sup> Wu,<sup>17b</sup> and Scott,<sup>17c</sup> it is noticeable that our strategy can directly and cleanly afford bisanthene from the corresponding bisanthryl in semi-gram scale.

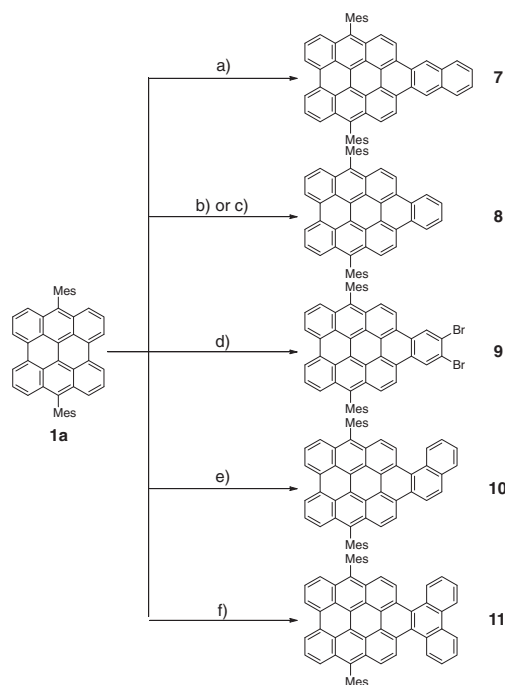
Our new method can also be applied to the synthesis of larger homologs, teranthene **2a**<sup>3a</sup> and quateranthene **3a**<sup>3c</sup> (Scheme 1). The MALDI-TOF mass spectra of the reaction mixture supported the formation of **2a** and **3a** (Figures S1a and S2a). Furthermore, the electronic absorption spectra of the reaction product after purification were consistent with the authentic spectra (Figures S1b and S2b).

The successful improvement of the synthesis of bisanthene by using the improved Scholl reaction enables us to explore the potential for building blocks toward polyperiacenes. The Diels–Alder cycloaddition of bisanthene at the bay region has brought about synthetic interest in building the skeleton toward large  $\pi$ -conjugated systems such as ovalene,<sup>9c,18a</sup> cylindrical hydrocarbons,<sup>17c,18b,18c</sup> and quinone-incorporated bisanthenes.<sup>18d</sup> In order to extend the scope of the cycloaddition reactions of bisanthene, we investigated the Diels–Alder cycloaddition of **1a** with several arynes, which can be generated in situ under mild conditions as dienophiles.

Various arynes generated from several precursors<sup>19</sup> are subjected to the Diels–Alder cycloaddition of **1a** followed by dehydrogenation to afford  $\pi$ -expanded bisanthenes in acceptable yields (Scheme 2). Naphthalene-*[b]*-annulated **7** and benzene-annulated **8** were obtained by gentle reflux of **1a** in toluene with naphthalene-2-diazonium-3-carboxylate and benzenediazonium-2-carboxylate, respectively. **8** was also obtained by gentle reflux of **1a** in THF with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate and cesium fluoride. Dibromobenzene-annulated **9** was obtained by treating **1a** and 1,2,4,5-tetrabromobenzene in refluxed toluene with *n*-BuLi. Naphthalene-*[a]*-annulated **10** and phenanthrene-annulated **11** were synthesized by treatment of **1a** and 1-bromonaphthalene or 9-bromophenanthrene in refluxed THF with excess NaNH<sub>2</sub>, respectively.

All reactions proceeded smoothly under mild conditions. It should be notable that the mono-addition product can be dominantly obtained even in the presence of the excess aryne precursor, in contrast to previous reports affording a mixture of mono- and double-addition products.<sup>18</sup> It seems that the milder reaction conditions, compared with the previous reactions performed under refluxed nitrobenzene at 240 °C<sup>9c,18a,18d</sup> or in a pressure vessel,<sup>17c,18b,18c</sup> would selectively lead to the mono-addition products. From these results, it is proved that arynes are useful dienophiles in the Diels–Alder cycloaddition with bisanthene to precisely expand  $\pi$ -systems in the lateral direction under a mild condition.

The optical properties of compounds **1a** and **7–11** recorded in CH<sub>2</sub>Cl<sub>2</sub> are summarized in Table 2. The electronic absorption spectra of these compounds show two characteristic absorption bands; the longest absorption band (*p* band: 550–700 nm); the second longest absorption band ( $\beta$  band: 300–420 nm) (Figures 1 and S8<sup>12</sup>). The *p* bands of **1a** and **7–11** have similar



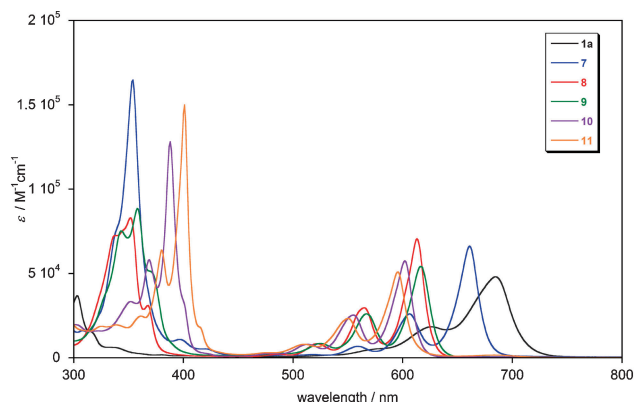
**Scheme 2.** Diels–Alder reaction of **1a** with several arynes. Reagents and conditions: a) 3-amino-2-naphthoic acid, isoamyl nitrite, toluene, reflux, 1 h, 39%; b) anthranilic acid, isopentyl nitrite, toluene, reflux, 1 h, 75%; c) 2-(trimethylsilyl)phenyl trifluoromethanesulfonate, CsF, THF, reflux, 1 day, 72%; d) *n*-BuLi, 1,2,4,5-tetrabromobenzene, toluene, reflux, 1.5 h, 51%; e) 1-bromonaphthalene, NaNH<sub>2</sub>, THF, reflux, 2 h, 49%; f) 9-bromophenanthrene, NaNH<sub>2</sub>, THF, reflux, 12 h, 40%.

**Table 2.** Optical and electrochemical<sup>a</sup> properties of **1a** and **7–11**

Compound	$\lambda_{\max}$ /nm	$\lambda_{\text{em}}$ /nm	$^{\text{ox}}E_{2,1/2}$ /V	$^{\text{ox}}E_{1,1/2}$ /V	$^{\text{red}}E_{1,1/2}$ /V	$^{\text{red}}E_{2,1/2}$ /V	$\Delta^{\text{redox}}E$ /V
<b>1a</b>	685	705	0.65	0.02	−1.66	−2.19 <sup>b</sup>	1.68
<b>7</b>	661	672	0.65	0.08	−1.68	−2.07	1.76
<b>8</b>	613	623	0.75	0.14	−1.76	−2.29 <sup>b</sup>	1.90
<b>9</b>	617	627	0.78	0.21	−1.70	−2.07 <sup>b</sup>	1.90
<b>10</b>	602	611	0.78	0.17	−1.77	−2.30 <sup>b</sup>	1.94
<b>11</b>	596	602	0.79	0.18	−1.80	−2.34 <sup>b</sup>	1.98

<sup>a</sup>V vs. Fc/Fc<sup>+</sup>, in 0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub>, scan rate 100 mV s<sup>−1</sup>, +25 °C. <sup>b</sup>Peak potentials.

shapes with vibrational fine structures, which can be assigned to the HOMO–LUMO transition. Consistent with the reported longest absorption bands of the laterally  $\pi$ -expanded bisanthenes,<sup>18d</sup> **7–11**, despite of larger size, also exhibited blue shifts in comparison with **1a**. The  $\pi$ -annulation at the bay region causes the increase in the HOMO–LUMO gap of **1a**, which is supported by the DFT calculation at the B3LYP/6-31G\*\* level.<sup>20</sup> The DFT calculation suggests that the  $\pi$ -annulation at the bay region of bisanthene stabilizes the HOMO level and destabilizes the LUMO level. The electronic perturbation given by  $\pi$ -annulations increases in order from naphthalene-*[b]*- to benzene-, naphthalene-*[a]*-, phenanthrene-, ethylene-annulation (Figure S5).<sup>12</sup>



**Figure 1.** Electronic absorption spectra of **1a** and **7–11** in  $\text{CH}_2\text{Cl}_2$ . For more detail, see Figure S8 in the Supporting Information.<sup>12</sup>

The redox properties of the laterally  $\pi$ -expanded bisanthenes **7–11** were examined by cyclic voltammetry. The redox potentials are summarized in Table 2 (see also Figure S4<sup>12</sup>). **7–11** basically possess four-stage redox properties and the electrochemically determined HOMO–LUMO gaps are well correlated with the optically determined HOMO–LUMO gaps.

In summary, we developed a facile synthetic method for anthenes from the corresponding anthracene oligomers by using an improved Scholl reaction. The simultaneous combination of all three components (DDQ,  $\text{Sc}(\text{OTf})_3$ , and Brønsted acids) plays a main role in the cyclization reaction of anthracene rings. The multiple formation of intramolecular C–C bonds in one step is highly advantageous to the preparation of bisanthenes, which enables us to explore the bay region reactivity with arynes. The lateral  $\pi$ -expansion of bisanthene under mild conditions is established by using the cycloaddition reaction of arynes. The combination of the two synthetic methods would lead to various size- and shape-controlled polyperiacenes, and further studies are now in progress in our group.

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