

# Synthesis and Photophysical Properties of Expanded Dehydrobenzoannulenoannulene Trefoils

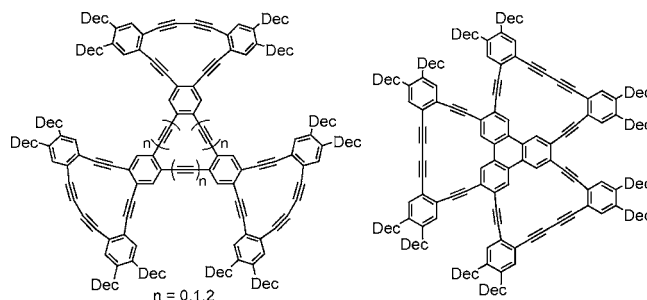
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## ABSTRACT



A sequential Sonogashira cross-coupling/Pd-mediated oxidative homocoupling strategy affords two-dimensional dehydrobenzoannulene trefoils containing different sizes of the central annulenic ring system. Use of these conditions instead of Cu-mediated homocoupling conditions yields a structural isomer possessing a triphenylene ([6]annulene) core. Noticeable differences in the absorption and emission spectra are observed depending upon the core unit.

Highly conjugated carbon-rich compounds<sup>1</sup> continue to receive considerable attention not only because of the fundamental science aspects<sup>2</sup> (e.g., aromaticity/antiaromaticity) of these aesthetically appealing compounds but also due to the interesting chemical and physical properties that these  $\pi$ -electron-rich species possess.<sup>3</sup> Our studies have focused on the synthesis and optoelectronic attributes of a particular subset of carbon-rich compounds named dehy-

drobenzoannulenes (DBAs).<sup>4</sup> We and others have shown that DBAs exhibit a myriad of technologically relevant properties including nonlinear optical activity,<sup>5</sup> two-photon absorption,<sup>6</sup> and liquid crystalline behavior,<sup>7</sup> among many others.<sup>8</sup> More recent work has turned to the investigation of increasingly larger and synthetically more complex systems (e.g., trefoils)

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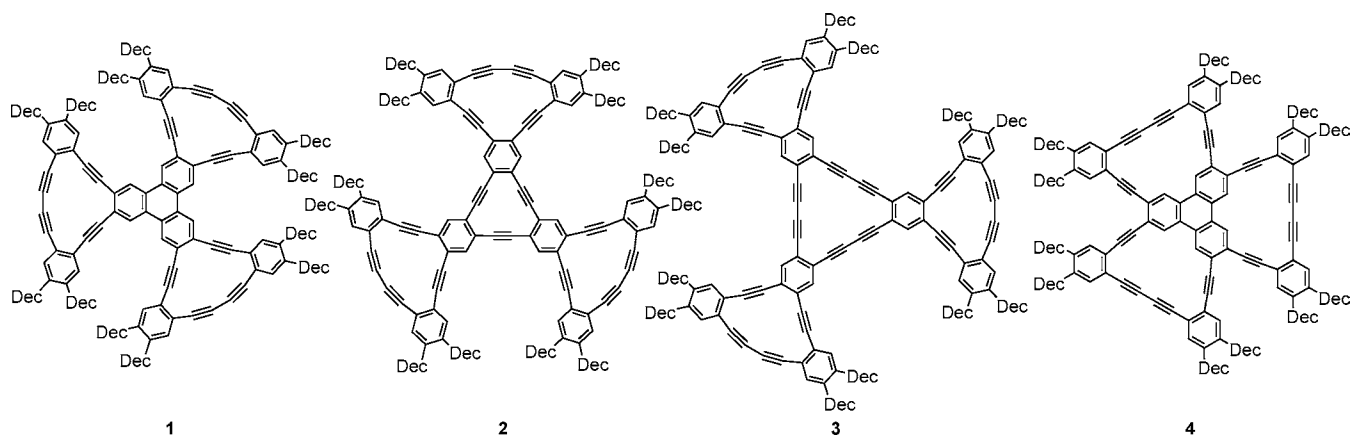
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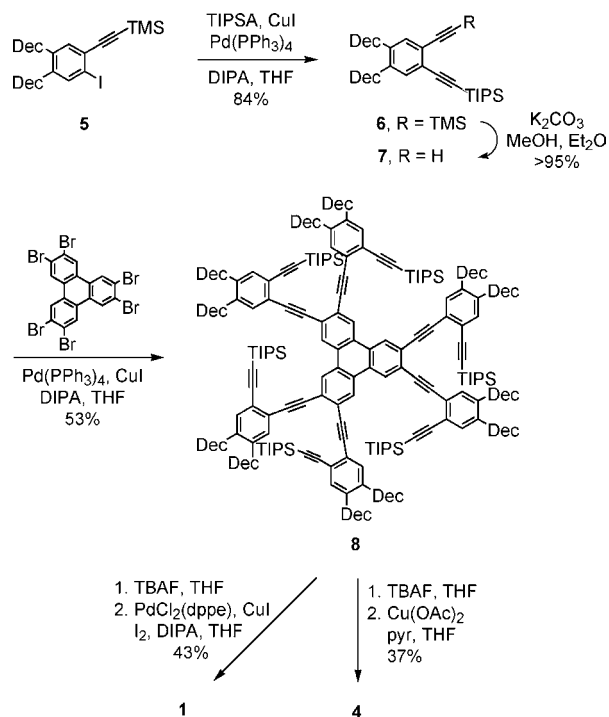


**Figure 1.** Target dehydrobenzoannulene trefoils **1–4**.

containing multiple fused DBAs.<sup>9</sup> In a vast majority of these molecules, the annulene rings have been the same size, typically 12-membered<sup>9b,d–f</sup> or 18-membered rings.<sup>9a,c</sup> We were curious to learn what effect, if any, that variation of the ring size of the central arene in a series of expanded molecular trefoils might have. To that end, we report herein the synthesis and optoelectronic properties of trefoil-shaped DBAs **1–3** possessing [6]-, [12]-, and [18]annulenes, respectively, as the central fused ring (Figure 1). In addition, we also present trefoil **4**, a structural isomer of **1**, prepared from a common intermediate via an alternative homocoupling procedure.

Given prior problems of expanded DBAs with poor molecule solubility,<sup>4a,9</sup> we designed our syntheses such that **1–4** incorporated 12 decyl units. Starting from **5**,<sup>9e</sup> Sonogashira cross-coupling of (triisopropylsilyl)acetylene (TIPSA) afforded differentially protected diyne **6** (Scheme 1). Protiodesilylation and a second Sonogashira reaction with hexabromotriphenylene<sup>10</sup> gave dodecayne **8** in a reasonable ca. 50% yield for the two steps. Molecular modeling suggested that once desilylated, the terminal alkynes were sufficiently close to one another that either trefoil **1**,

**Scheme 1.** Synthesis of Triphenylene Core Trefoils **1** and **4**



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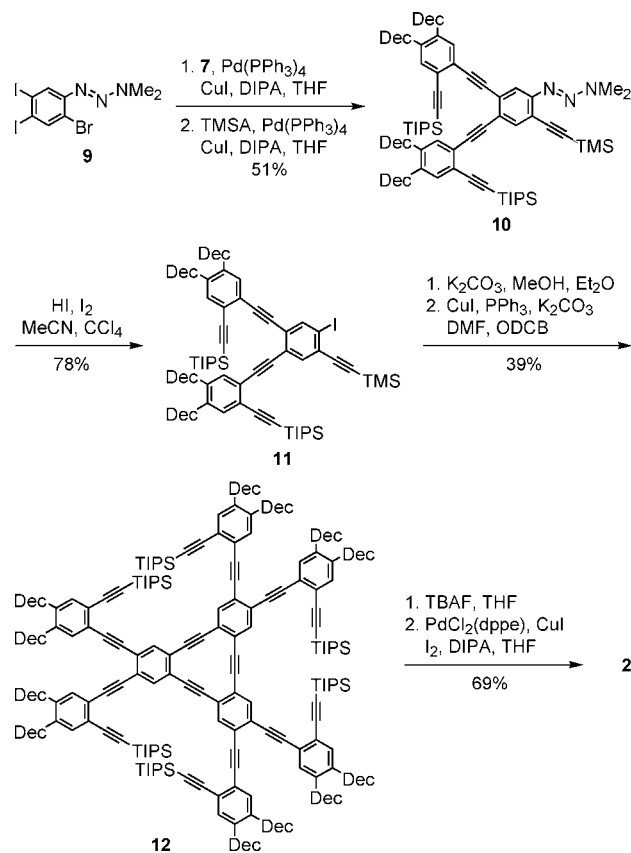
possessing three 14-membered DBA rings, or **4**, containing three 18-membered rings, could form during the homocoupling reaction. We recently reported reaction conditions that made it possible to discriminate between annulene ring size, depending upon ring strain in the organometallic intermediate prior to reductive elimination.<sup>11</sup> Gratifyingly, desilylation of **8** with TBAF and subsequent treatment with catalytic PdCl<sub>2</sub>(dppe) and stoichiometric I<sub>2</sub> as oxidant furnished a single product. Conversely, use of excess Cu(OAc)<sub>2</sub> in the

(11) (a) Marsden, J. A.; Miller, J. J.; Haley, M. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1694–1697. (b) Marsden, J. A.; Miller, J. J.; Shirtcliff, L. D.; Haley, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 2464–2476.

homocoupling step afforded a sole yet different compound. We have provisionally assigned these as trefoils **1** and **4**, respectively, based on the upfield NMR chemical shift of the triphenylene protons of **4** ( $\delta$  9.20 for **1** vs 8.29 for **4**, starting from 8.72 for **8**) which lie in the shielding cone of the aromatic 18-membered  $\pi$ -system,<sup>12</sup> as well as based on the aforementioned “organometallic intermediate” argument. Simply put, the *cis*-oriented Pd(dppe) intermediate that could possibly lead to the 18-membered ring is too highly strained to form, whereas the analogous “*trans*-like” dimeric Cu species leading to **4** is relatively strain-free. The reverse argument applies for **1**: the *cis*-oriented Pd(dppe) intermediate that leads to the 14-membered ring is relatively strain-free, whereas a “*trans*-like” dimeric Cu-species leading to **1** is highly strained.<sup>11</sup>

Preparation of trefoil **2** began with known triazene **9** (Scheme 2).<sup>9c</sup> Sequential Sonogashira reactions with 2

**Scheme 2.** Synthesis of [12]DBA Core Trefoil **2**



equiv of **7** and then excess TMSA provided triazene **10**, which was followed by triazene conversion to iodoarene **11** using HI/I<sub>2</sub> at rt.<sup>13</sup> Protodesilylation and subsequent

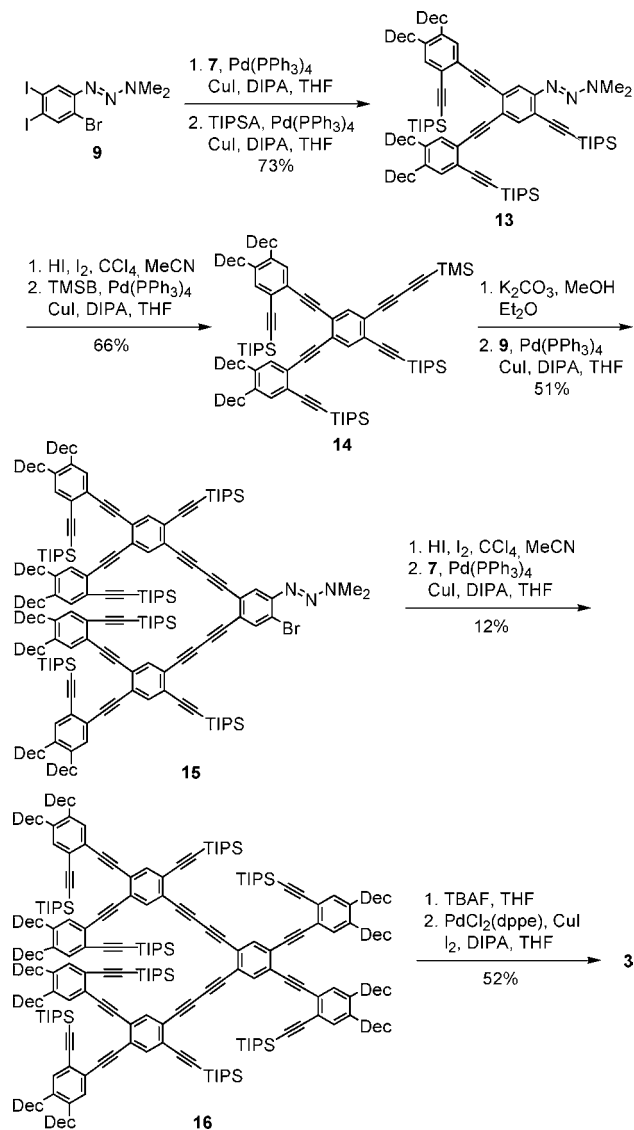
(12) A model system containing a single 18-membered subunit of **4** exhibited an analogous upfield shift of the intra-annular protons: Jones, C. S. Postdoctoral Report, University of Oregon, 2005.

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cyclotrimerization using the conditions of Iyoda<sup>14</sup> furnished precursor **12** in 39% yield. Removal of the six TIPS groups by TBAF followed by Pd-mediated homocoupling under pseudohigh dilution conditions gave **2** in a respectable 69% yield.

Starting again with triazene **9**, sequential Sonogashira reactions with 2 equiv of **7** and then excess TIPSAs provided **13** (Scheme 3). Triazene conversion as before and then cross-

**Scheme 3.** Synthesis of [18]DBA Core Trefoil **3**



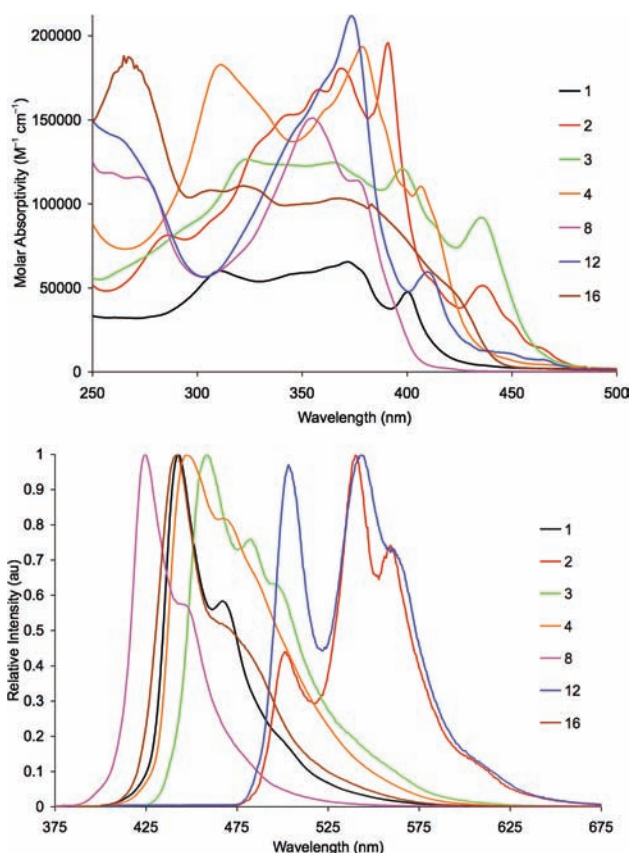
coupling with (trimethylsilyl)butadiyne gave heptyne **14**. Selective protodesilylation with K<sub>2</sub>CO<sub>3</sub> in MeOH/THF followed by Sonogashira reaction with another 1 equiv of **9** afforded **15**. While triazene iodide conversion with HI/I<sub>2</sub> occurred in similar fashion, subsequent cross-coupling with excess **7** proceeded poorly such that the overall yield of the

(14) Iyoda, M.; Sirinintasak, S.; Nishiyama, Y.; Vorasingha, A.; Sultana, F.; Nakao, K.; Kuwatani, Y.; Matsuyama, H.; Yoshida, M.; Miyake, Y. *Synthesis* **2004**, 1527–1531.

two steps furnished precursor **16** in no more than 12%. Nonetheless, a final desilylation with TBAF and subsequent Pd-mediated homocoupling gave **3**.

As desired, all four trefoils possessed sufficient solubility such that they could be easily purified by column chromatography and their complete spectral data secured. Other than the aforementioned triphenylene proton shifts, NMR analysis of **1–4** did not provide sufficient detail about core size differences. The periphery arene protons of the trefoils did exhibit lower field shifts compared with the corresponding precursors ( $\Delta\delta$  0.05–0.15 ppm), typical of the weak aromatic character of the fused 14 and/or 18  $\pi$ -electron systems.<sup>15</sup> Similar to our previous results of purely hydrocarbon expanded DBAs, no evidence for self-association in solution was observed.

More instructive are the electronic absorption and emission spectra of trefoils **1–4**. As shown in Figure 2 (top), **2–4**



**Figure 2.** Electronic absorption (top) and fluorescence (bottom) spectra of trefoils **1–4** and their precursors **8**, **12**, and **16**.

red-shift ca. 30 nm to lower energy compared to their acyclic precursors, whereas the shift of **1** is more modest (ca. 10 nm). Interestingly, trefoils **2** and **3** appear to have

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the same low energy band at 436 nm. Closer inspection of **2** (as well as precursor **12**) reveals the characteristic vibronic spectral pattern of the antiaromatic [12]DBA core,<sup>9e,16</sup> with discernible shoulders at 450 and 470 nm, a spectral feature lacking in **3**.

The most notable differences arising from variation of core size are depicted in the emission spectra in Figure 2 (bottom) and Table 1. Trefoils **1**, **3**, and **4** possess maxima roughly

**Table 1.** Quantum Yields of Trefoils **1–4** and Their Precursors **8**, **12**, and **16**

compd	quantum yield <sup>a</sup> (%)	stokes shift (nm/cm <sup>-1</sup> )
<b>1</b>	15	43/2430
<b>2</b>	2.7	66/3020
<b>3</b>	16	22/1100
<b>4</b>	16	40/2200
<b>8</b>	9.1	48/3010
<b>12</b>	9.9	93/4510
<b>16</b>	25	21/1130

<sup>a</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> and determined by comparison 9,10-diphenylanthracene as reference.

20 nm red-shifted compared to their precursor molecules, emitting in the general range of 400–550 nm. In contrast, trefoil **2** and precursor **12** emit at lower energy (475–625 nm), with the spectra exhibiting the vibrational splitting often observed for [12]DBA derivatives.<sup>9d,e</sup> While the additional alkyne units in **3** afford a slightly longer linear conjugation pathway compared to **2**, the ca. 90 nm lower energy  $\lambda_{em}$  maximum of **2** suggests that the longest conjugation length does not dictate the fluorescence properties of these trefoil-shaped hydrocarbons; instead, it is the intrinsic spectral features of the particular core unit that predominate.

In summary, we have synthesized a series of expanded annulene derivatives that possess different sizes of the central ring system. Optoelectronic measurements clearly show that the absorption and emission properties of the trefoil-shaped molecules can vary significantly depending on use of an aromatic (**1**, **3**, **4**) or antiaromatic (**2**) annulene core. Further studies on additional expanded annulene derivatives will be reported in due course.

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**Supporting Information Available:** Experimental details and spectroscopic data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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