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Semi-fused hexaphenyl hexa-*peri*-hexabenzocoronene: a novel fluorophore from an intramolecular Scholl reaction

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ABSTRACT

A semi-fused hexaphenyl hexabenzocoronene derivative (hexaphenyl-1/2HBC) was discovered and isolated from an intramolecular Scholl reaction of an oligo(ethyleneglycol) substituted hexabiphenylbenzene. This new derivative exhibits blue-shifted λ_{em} and significantly enhanced fluorescence in dichloromethane compared to the completely cyclized hexaphenyl-HBC derivative.

Hexa-*peri*-hexabenzocoronenes (HBCs) are an interesting class of polycyclic aromatic hydrocarbon molecules that can be regarded as disc-like, small graphene sections. Prompted by their interesting structures and properties, HBC derivatives have aroused intense interest in synthesis and applications in organic electronics. Their conjugated 'superbenzene' surfaces tend to strongly aggregate into columnar nanostructures with enhanced charge carrier mobility compared to other discotic liquid crystalline materials.[1]

Harsh reaction conditions[2] were used to prepare HBC molecules until Müllen and co-workers demonstrated that mild Scholl condensation[3] conditions, either $CuCl_2/AlCl_3/CS_2$ or $FeCl_3/CH_3NO_2$, can be used to prepare HBCs conveniently from hexaphenylbenzene precursors.[4,5] This protocol allowed their subsequent breakthrough syntheses of extended 2D graphene nanosheets.[6,7] The reaction mechanism, however, was not clarified. In the chemical literature, two possible reaction mechanisms were considered for the Scholl reaction, including the arenium cation mechanism and radical cation mechanism.[8] Aside from that, only few computational studies of the two mechanisms have been reported.[9,10] The aryl–aryl dehydrogenative coupling reaction was concluded to occur intramolecularly in separate steps, as evidenced experimentally from isolation of reaction intermediate **2** with four new carbon–carbon bonds in 10% yield (Scheme 1a).[5] So far, this has been the only report of isolated intermediate from Scholl condensation of an all-carbon hexaphenylbenzene precursor **1**.[11] In another case, Scholl condensation of programmed all-carbon oligophenylene precursors **3**–**4** generated two partially fused reaction intermediates **5**–**6** (Scheme 1b).[12] Steric hindrance and the stability of the radical cation were suggested to render the preferential formation of **5** and **6**, respectively. A recent report on the preparation of nitrogen-functionalized HBCs involving pyrimidines showed that the metal catalyst might interact with the substrate to terminate the Scholl reaction halfway: condensation of 1,2-dipyrimidyl-3,4,5,6-tetra(4-*tert*-butylphenyl)benzene **7** in $FeCl_3/MeNO_2$ provided fused-ring species **8** which cannot be further converted to HBC analog **9** (Scheme 1c).[13] Further, several reports indicated that only properly designed hexaphenylbenzene precursors can undergo Scholl condensation to give alkoxy-substituted HBCs.[14–17] Due to the lack of generality of Scholl reaction conditions to produce different HBCs and elusiveness of the reaction mechanisms, reaction intermediates are of great significance to advance our understanding and to guide the synthetic formulation of HBC molecules and HBC-based conjugated polymers. In this Letter, we report on the synthesis and photophysical properties of the unprecedented HBC intermediate **11** from Scholl condensation of an all-carbon hexabiphenylbenzene precursor **10** (Scheme 2).

Recently, during our investigation of Scholl reaction to synthesize amphiphilic hexaphenyl-HBC **12** using $FeCl_3/MeNO_2$, we found that a compound **11** with molecular weight corresponding to three newly formed carbon–carbon bonds (hexaphenyl-1/2HBC) was always observed by MALDI-MS. This interesting finding prompted us to isolate **11** and study the reaction to further investigate its nature and unusual product formation. The oxidative cyclodehydrogenation of precursor **10** (50 mg) was conducted under concentrated (2.6 mM), medium (0.6 mM), and dilute (0.4 mM) conditions, using 45 equiv of $FeCl_3$. When the highest concentration (2.6 mM) was applied, after 45 min, the starting material **10** was found to

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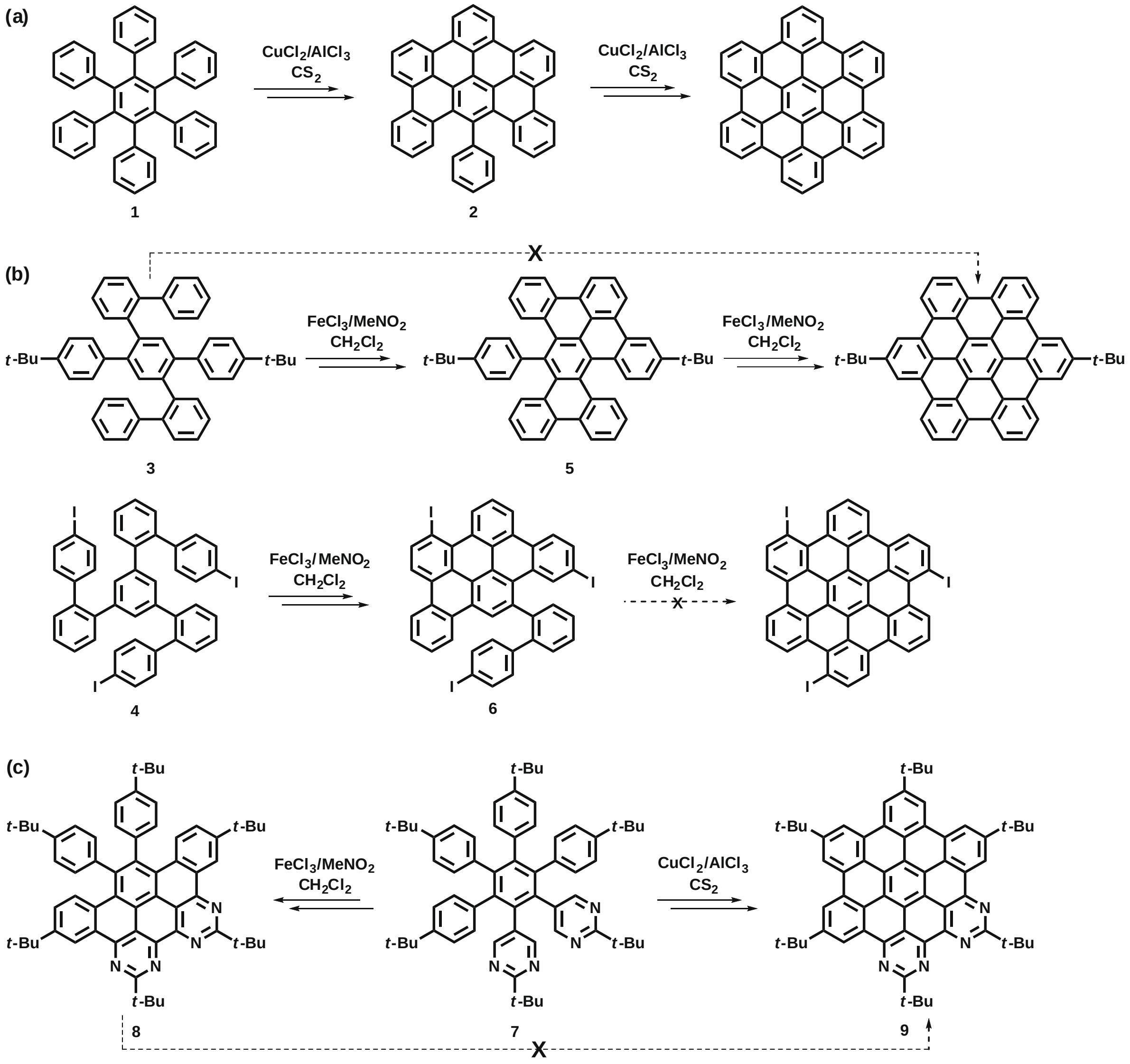
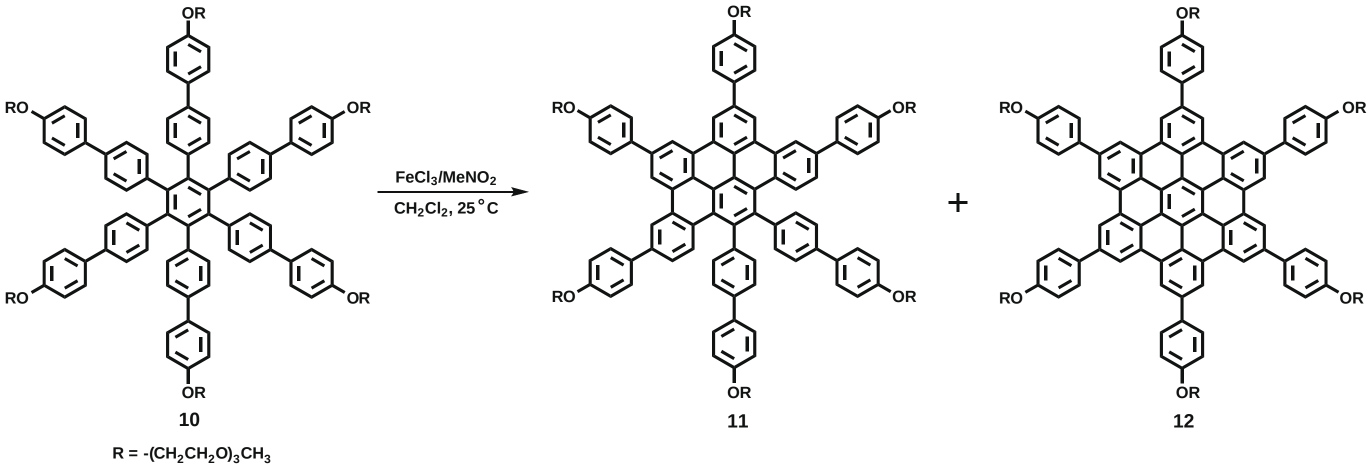


Scheme 1. HBC intermediates in the Scholl condensation reactions.



Scheme 2. Syntheses of hexaphenyl-1/2HBC **11** and hexaphenyl HBC **12**.

transform primarily into completely cyclized hexaphenyl HBC **12** (m/z = 1952) along with oligomer products from intermolecular condensation as well as a minor amount of incompletely cyclized mixture product (m/z = 1958 amu) being the only clearly identified

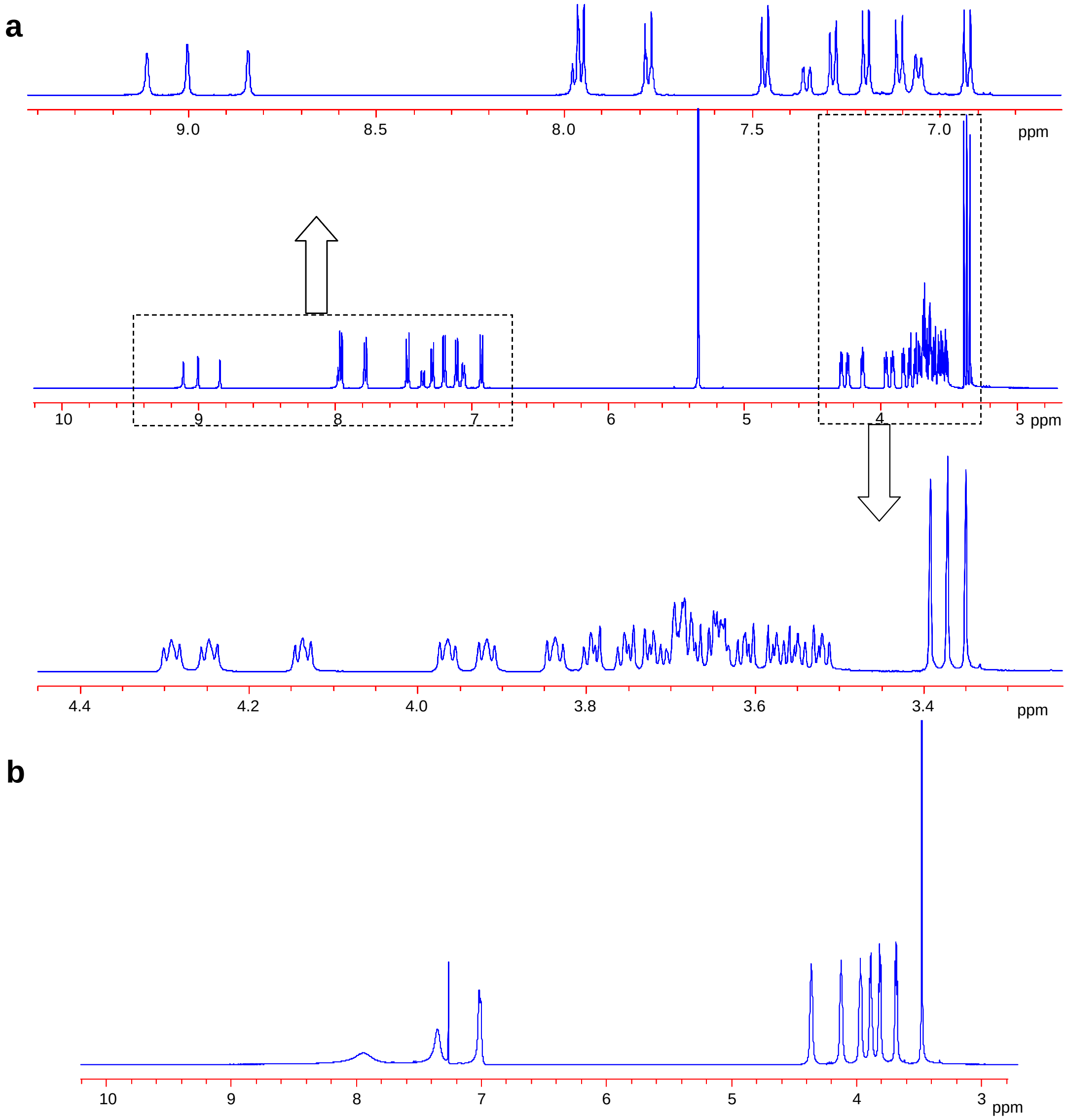


Figure 1. (a) ^{1}H NMR spectrum of hexaphenyl-1/2HBC **11** (CD_2Cl_2, 500 MHz, 20 °C) after purification; (b) ^{1}H NMR spectrum of hexaphenyl-HBC **12** ($CDCl_3$, 500 MHz, 20 °C).

species above the detection limit of MALDI. We found that the transformation into oligomer products can be eliminated by decreasing the substrate concentration during the reaction. It was possible to separate the incompletely cyclized product and precursor residues from **12** by silica gel column chromatography using a more polar solvent (CH_2Cl_2/CH_3OH, 49/1, v/v), while by

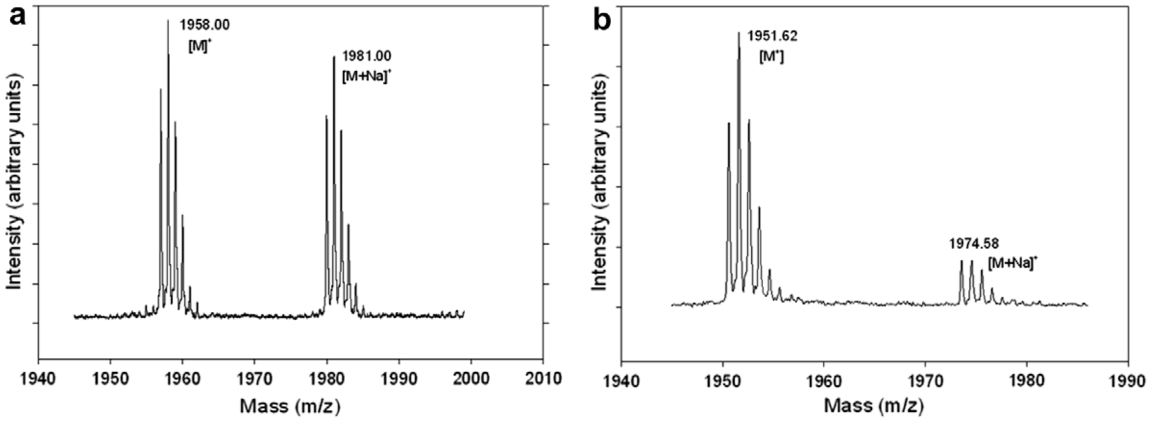


Figure 2. Isotopic envelop of (a) hexaphenyl-1/2HBC **11** and (b) hexaphenyl-HBC **12** by MALDI-MS.

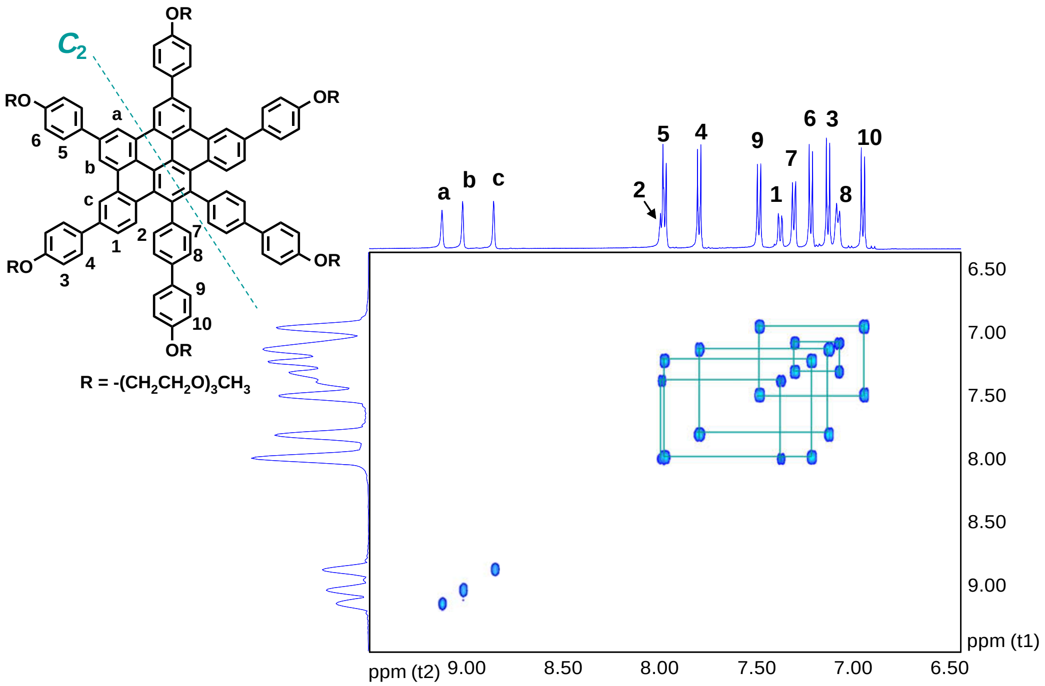


Figure 3. ^1H–^1H COSY NMR spectrum (CD_2Cl_2, 500 MHz, 20 °C) of hexaphenyl-1/2HBC **11**.

switching to a carefully performed chromatography using a less polar solvent (CH_2Cl_2/acetone, 3/1, v/v) it was possible to separate the $m/z = 1958$ amu product from the precursor residues. An incompletely cyclized product with m/z of 1958 amu was also obtained from medium and dilute concentration reactions in 17–20% yield. Medium concentration also provided completely cyclized **12** in 44–60% yield.

The incompletely cyclized product was a pure substance whose structure was determined to be **11** using ^1H NMR (Fig. 1), ^{13}C NMR, MALDI-MS (Fig. 2), and ^1H–^1H COSY (Fig. 3) experiments. The single isotopic envelop of **11** at m/z 1958.00 $(M)^+$ and 1981.00 $(M+Na)^+$ compared to that of hexaphenyl-HBC **12** at m/z 1951.62 $(M)^+$ and 1974.58 $(M+Na)^+$ revealed a mass difference of 6, which is in agreement with dehydrogenation of 6 protons due to three carbon-carbon bond formation. The covalent connectivity of compound **11** was unambiguously determined by ^1H–^1H COSY NMR. Figure 3 shows the enlarged aromatic areas of the COSY NMR spectrum. There are only three aromatic singlets (δ 9.09, δ 8.98, and δ

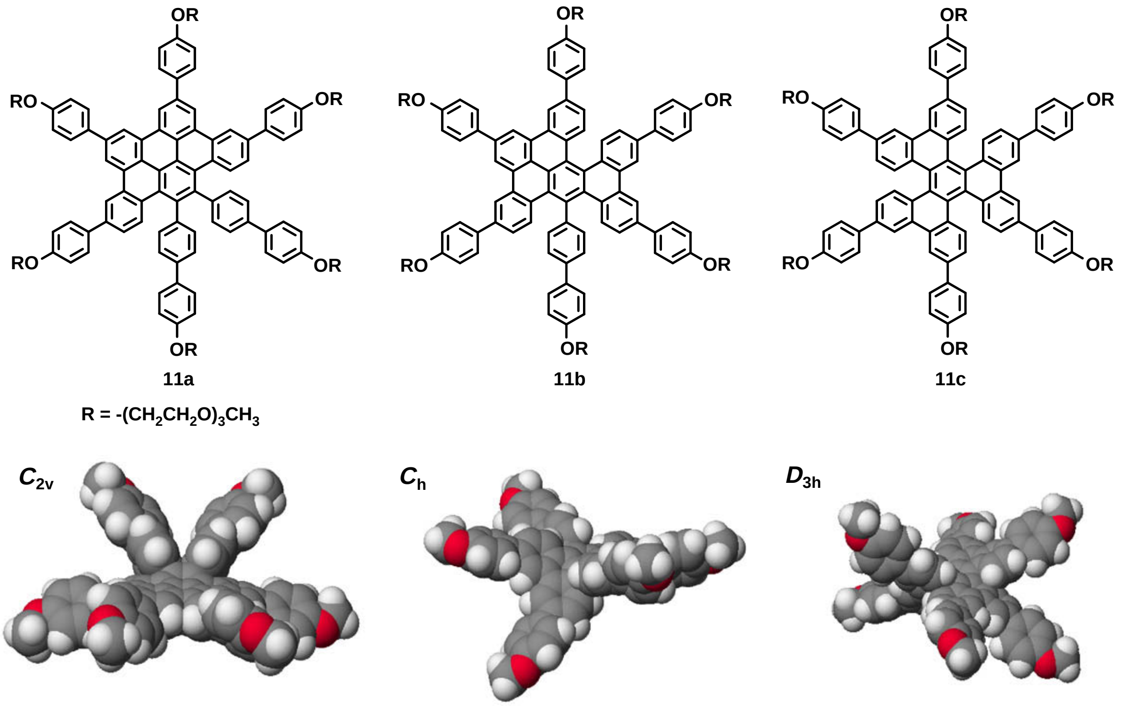


Figure 4. Space-filling models of three possible constitutional isomers of **11** where methoxy oligophenylenes were used for calculation simplicity. The conformations shown are energy-minimized structures.[18]

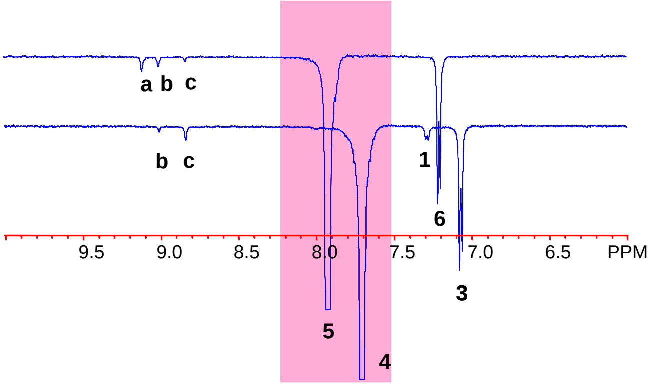


Figure 5. NOESY1D NMR spectrum ($CDCl_3$, 500 MHz, 20 °C) of hexaphenyl-1/2HBC **11** (the colored resonance regions were irradiated selectively).

Table 1
Approximate energy of three constitutional isomers of **11** based on MM2 calculations[18]

Isomer	$-\Delta H$ (kcal/mol)
11(a)	122.8
11(b)	130.1
11(c)	140.5

8.82) deshielded to the lowest field, corresponding to the isolated *ortho*-hydrogens of the fused ring. Among three possible constitutional isomers of **11** in Figure 4, the only qualified structure is semi-fused isomer **11**(a) that possesses a C_2 symmetry axis. These three singlets integrate to six hydrogens, and the remaining ten aromatic doublet signals integrate to 36 hydrogens in total. The resonance correlated doublets at δ 7.97 and δ 7.35 each integrate to two hydrogens and differ from the other eight doublets each integrating to four hydrogens. These two doublets correspond to the two sets of neighboring hydrogens of the fused ring, while the eight doublets were assigned to the hydrogens of the eight uncyclized, free-rotating phenyl rings. The NOESY1D, CH COSY (HMBC-HMQC), and 135° DEPT NMR experiments made it possible to completely assign the aromatic protons of **11** based on the proposed structure. Key correlations of singlets a, b, c and doublets 1, 3–6 are shown in Figure 5. The complete assignments of all aromatic protons were summarized in Figure 3. The proposed C_{2v} symmetry of **11** was also confirmed by the observation of three sets of alkoxy signals for the oligo(ethylene glycol)ether chains as shown in Figure 1.

To better understand the formation of semi-fused structure **11**, modeling studies were performed to calculate the relative stabilities of three constitutional isomers **11(a)**–**(c)** (Table 1, Fig. 4). Results indicate that isomer **11(a)** has the lowest energy compared to isomers **11(b)** and **11(c)**. Therefore, the observed product is also the thermodynamically most favored product among three isomers.

The unexpected discovery of hexaphenyl-1/2HBC **11** also prompted us to further investigate whether **11** is a kinetically favored precursor of hexaphenyl-HBC **12** generated during the stepwise cyclodehydrogenation reaction by treatment with $FeCl_3$, or whether **11** is a thermodynamically stable product formed inde-

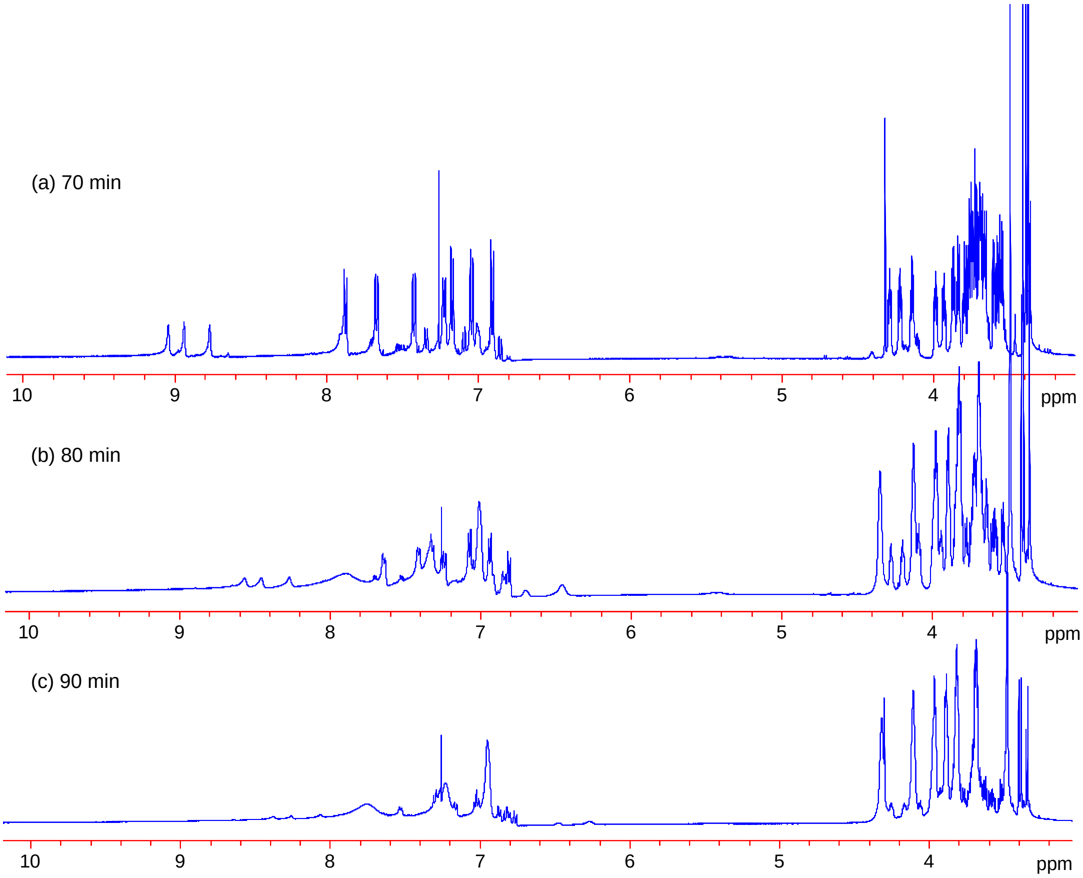


Figure 6. Comparison of ^1H NMR spectra of crude condensation reaction mixtures upon MeOH quenching for cyclodehydrogenation of **10** after 70 min, 80 min, and 90 min, respectively ($CDCl_3$, 500 MHz, 20 °C). Condensation conditions: 50 mg **10**, 1.13 mmol $FeCl_3$, 4.8 mL $MeNO_2$, 40 mL CH_2Cl_2, 25 °C; quenching with 40 mL MeOH.

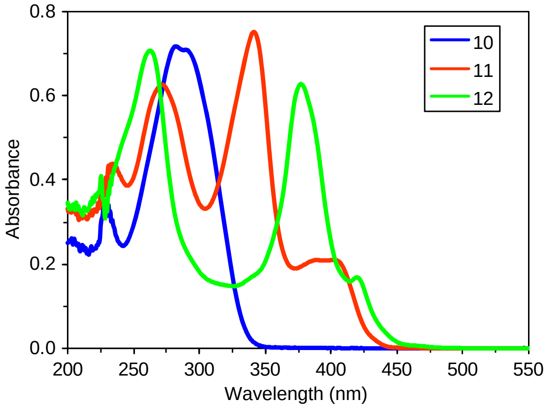


Figure 7. UV–vis absorption spectra of **10**–**12** in dichloromethane at 25 °C. The spectra are normalized to 5.1 μM concentration.

Table 2
Absorption maxima and extinction coefficients of **10**–**12**

Compd	λ_{max} (abs), nm	ε, M^{-1} cm^{-1}
10	229.0	6.90×10^4
	282.0	1.41×10^5
11	205.5	6.47×10^4
	234.0	8.61×10^4
	271.5	1.23×10^5
	341.5	1.47×10^5
	389.5	4.12×10^4
	402.5	4.12×10^4
12	225.5	8.04×10^4
	262.5	1.39×10^5
	377.0	1.24×10^5
	419.5	3.31×10^4

pendent of **12**. ^{1}H NMR was used to monitor the product distribution of three individual reactions under the medium concentration condition with varied reaction times: 70 min, 80 min, and 90 min (Fig. 6). The reaction time within this 20 min window had a dramatic effect on the product distribution. The majority of **11**, which appeared to be the main product in the ^{1}H NMR spectrum at 70 min, converted to fully cyclized **12** at 90 min. However, cyclodehydrogenation reaction pathways are known to be complex:[13] the sensitivity of the reaction time, oxidant loading, and addition rate, as well as reaction concentration all lead to the difficulty in achieving accurate control of the product distribution. However, the comparison data demonstrate that **11** is a kinetically favored reaction intermediate instead of a thermodynamically stable product. To support this statement further, purified compound **11** was subjected to Scholl condensation reaction to confirm that **11** can be converted to completely cyclized **12**. ^{1}H NMR and ESI-MS results revealed that by using 22.6 equiv of $FeCl_3$, the majority of **11** was transformed into **12** after 40 min. Thus, we conclude that **11** is indeed a Scholl reaction intermediate. Although the generation of semi-fused HBC structure had been recently reported in the form of a nitrogen-containing HBC, such analog was shown to be a thermodynamically stable product that cannot undergo further transformation into the fully cyclized structure.[13]

The semi-fused **11** provides an opportunity to compare it with **12** for investigating the potential interesting photophysical properties and applications of semi-HBC structures. The UV–vis spectra of **10**–**12** in CH_2Cl_2 are presented in Figure 7, and the absorption maxima (λ_{max}) and molar extinction coefficient (ε) are collected in Table 2. Based on the spectra, the absorption of nonplanar **11** has two distinct bands in the UV region (245–305 nm, 305–370 nm). These two bands provide the characteristic vibronic spectral pattern responsible for the chromophore nature and planarity of **11**, respectively.[19,20] The absorption maxima around 272 nm is due to the oligophenylene chromophore, and the absorption in the other UV region around 342 nm is due to the planarization of the oligophenylene core to generate the semi-fused ring with added conjugation. Similarly, in the case of **12**, the absorption in the UV region (230–325 nm) represents the oligophenylene chromophore. The next absorption maxima of **12** (377 nm, 1.24×10^5 M^{-1} cm^{-1}) is bathochromically shifted compared to that of **11** (342 nm, 1.47×10^5 M^{-1} cm^{-1}) with a slight decrease in the absorption intensity upon extension of the conjugation. For comparison, the absorption spectrum of the reference compound **10** is also shown in Figure 7, which contains only one distinct UV band (240–350 nm) corresponding to its nonplanar polyphenylene chromophore as that in **11** and **12**.

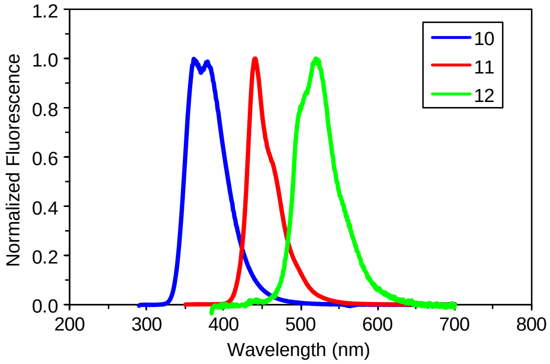


Figure 8. Normalized fluorescence spectra of **10**–**12** in dichloromethane (5.1 μM, 25 °C). The excitation wavelengths were set to the λ_{max} (abs) of each compound (**10**, 282 nm; **11**, 341 nm; **12**, 377 nm).

The fluorescence spectra of **11** and **12** generally lacked fine features possibly due to the high concentration used for the excitation experiments.[21] As shown in Figure 8, the emission maxima of **11** and **12** exhibited bathochromic shifts compared to that of precursor **10** in dichloromethane (**10**: λ_{em} = 370 nm, colorless; **11**: λ_{em} = 441 nm, Φ_F = 0.28, yellow-green; **12**: λ_{em} = 520 nm, Φ_F = 0.08, yellow). The fluorescence quantum yield of **11** is markedly higher than that of **12**. Interestingly, the solubility of **11** was found to be lower than that of **12**. The finding of the non-heteropolyaromatic, semi-fused **11** not only supports the stepwise Scholl condensation pathway leading to HBCs demonstrated earlier by Müllen and co-workers,[5] but also offers a new generation of conjugated fluorescent molecules. We imagine that introduction of such unique structures into polymer films would create new opportunities for developing optical and electronic materials from semi-fused HBCs.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.04.103.

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