

# Three-Fold Scholl-Type Cycloheptatriene Ring Formation around a Tribenzotriquinacene Core: Toward Warped Graphenes

Ho-Wang Ip,<sup>†</sup> Chun-Fai Ng,<sup>†</sup> Hak-Fun Chow,<sup>\*,†</sup> and Dietmar Kuck<sup>\*,‡</sup>

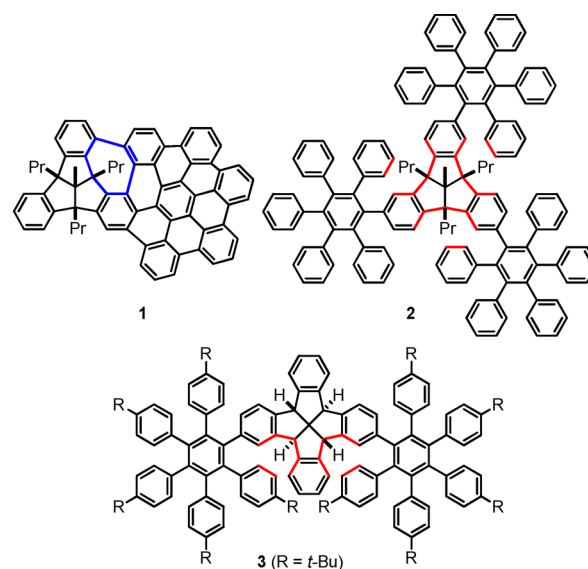
<sup>†</sup>Department of Chemistry, Institute of Molecular Functional Materials, and The Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, Hong Kong

<sup>‡</sup>Department of Chemistry and Center for Molecular Materials (CM2), Bielefeld University, 33615 Bielefeld, Germany

**S** Supporting Information

**ABSTRACT:** A nonplanar polycyclic aromatic compound **6** bearing a tribenzotriquinacene (TBTQ) core merged with an *o,p,o,p,o,p*-hexaphenylene belt was prepared and characterized by NMR spectroscopy and X-ray crystallography. The key synthesis step involves three Scholl-type cycloheptatriene ring formation steps of the 1,4,8-tris-(3',4'-dimethoxyphenyl)-TBTQ derivative **5**. The bridging of each of the three TBTQ bays by 1,2-phenylene units in compound **6** gives rise to an unusual wizard hat shaped structure, which represents a promising key intermediate for the construction of nonplanar nanographene molecules bearing a TBTQ core.

Polycyclic aromatic compounds (PACs) possessing a curved  $\pi$ -surface have aroused immense interest for decades due to their strained structures and unusual properties.<sup>1</sup> Curved PACs in the forms of spheres, tubes, hemispheres, and saddles are well-known morphologies of nanographenes, and their applications have been well-documented.<sup>2</sup> These curved molecules are mostly prepared by “bottom-up” strategies because they offer better product homogeneity and higher morphological control. Generally, the curved nature of PACs can be induced by the presence of nonhexagonal rings<sup>3</sup> or by steric crowding between substituents in a congested PAC skeleton.<sup>4</sup> Among the many synthetic protocols, the Scholl reaction<sup>5,6</sup> is the most effective method to stitch a delicately designed, loosely  $\pi$ -conjugated polyaryl ring system to the curved PAC at the final stage of the synthesis. The scope of the original Scholl method, which involved mostly hexagonal ring formation, has been optimized and expanded by Müllen<sup>7</sup> and King.<sup>8</sup> In contrast, there are only a few successful examples of employing the Scholl conditions in promoting heptagon ring formation. Several curved PACs prepared via the formation of cycloheptatrienyliene rings had been reported by Itami<sup>3g,k</sup> and Duroła.<sup>4f</sup> Pursuing an early idea to use tribenzotriquinacene (TBTQ) or fenestrindane cores to construct warped graphene cuttings,<sup>9</sup> one of us recently disclosed the successful synthesis of the curved PAC **1** based on a single cycloheptatriene ring formation around a TBTQ core (Figure 1).<sup>10</sup> However, multiple cycloheptatriene ring formation of the TBTQ derivative **2**<sup>11</sup> or fenestrindane congener **3**<sup>12</sup> under similar Scholl conditions failed. In the former case, unfavorable crowding and/or poor solubility of the partially fused intermediates may have prevented the desired multiple ring



**Figure 1.** Successful (blue bonds) bay-bridging cycloheptatriene ring formation of the TBTQ-merged hexa-*peri*-hexabenzocoronene **1** and unsuccessful (red bonds) cycloheptatriene ring formation of the TBTQ precursor **2** and the fenestrindane precursor **3**.

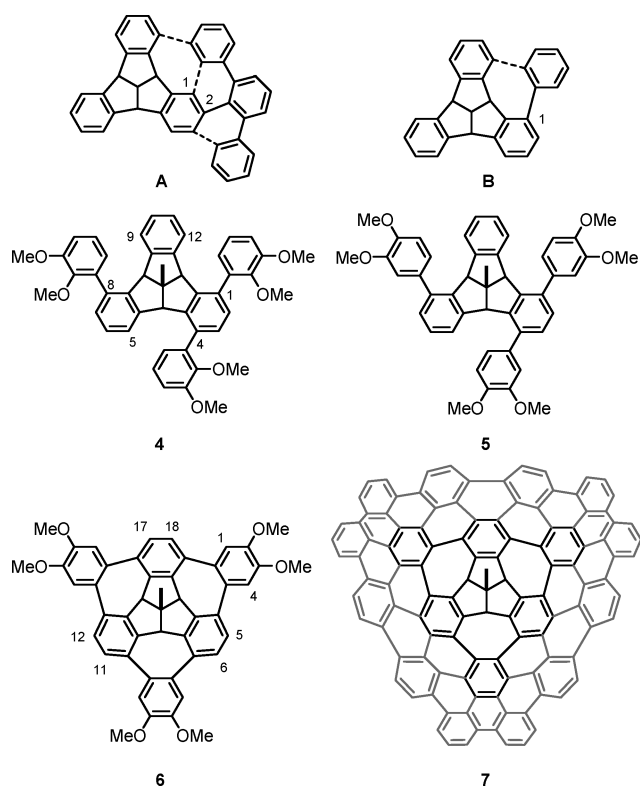
fusion, while in the latter the failure was attributed to steric inhibition when placing the bulky *tert*-butyl groups into the bay areas of the PAC unit.

Conceptually, a 2'-*m*-terphenyl residue at the C-2 position of the TBTQ skeleton (A in Chart 1) appears to be the minimum prerequisite to site a phenyl ring into the to-be-bridged bay region, although such an approach would create entropic penalty against cycloheptatriene ring formation due to the presence of two rotatable aryl–aryl bonds. On the other hand, the entropic advantage of a conformationally preorganized phenyl substituent placed suitably at the C-1 position (B in Chart 1) may promise successful bridging of the bay by Scholl-type cyclization. In this contribution, we present the successful synthesis of two 1,4,8-tris(dimethoxyphenyl)-TBTQ derivatives, **4** and **5**, the latter of which underwent an unprecedented 3-fold Scholl-type cycloheptatriene ring formation, leading to the successful synthesis of the nonplanar PAC **6**. Hence, the placement of aryl groups at the various bay

Received: June 7, 2016

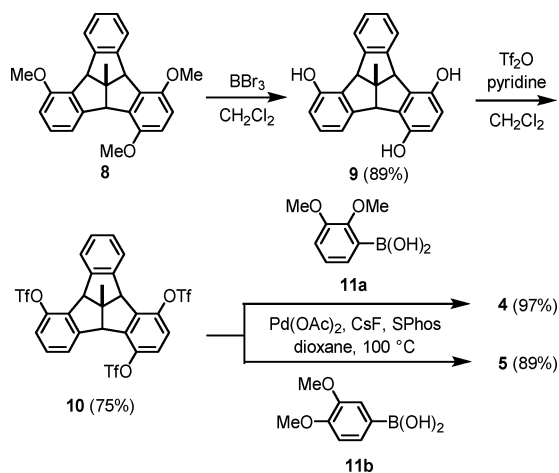
Published: August 1, 2016

Chart 1. Strategies (A, B) and Progress (4–6) for TBTQ Bay Bridging toward Warped Graphene (7)

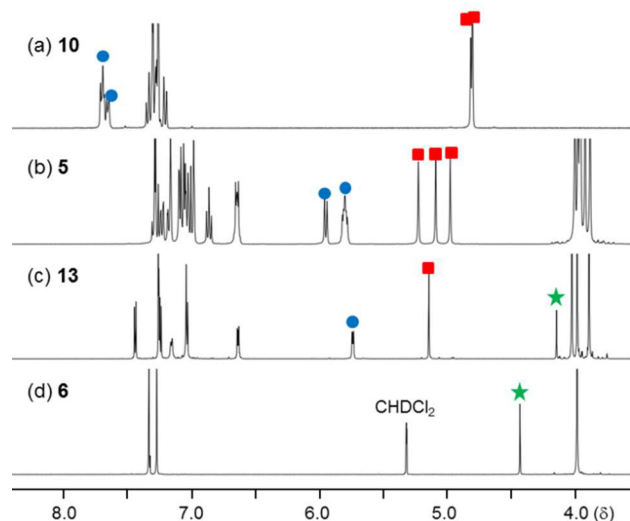


positions did indeed promote the Scholl reaction. The resulting wizard hat-shaped molecule **6**, having methoxy groups on the rim, can serve as a key intermediate toward the synthesis of further  $\pi$ -extended nonplanar nanographenes such as compound **7**.<sup>9,13</sup>

1,4,8-Trimethoxy-12D-methyltribenzotriquinacene **8**, a key intermediate for the preparation of compounds **4** and **5**, was prepared via the standard regiocontrolled double-cyclization method reported previously by us (Scheme 1).<sup>9c,14,15</sup> This compound was then subjected to demethylation with boron tribromide to give the corresponding trihydroxy-TBTQ derivative **9** in 89% yield. Subsequent reaction of **9** with triflic

Scheme 1. Synthesis of 1,4,8-Triaryl-Substituted TBTQ Derivatives **4** and **5**

anhydride gave the TBTQ-tris-triflate **10** in 75% yield. Based on the previous findings that electron-rich aryl groups could facilitate the classical Scholl reaction,<sup>8</sup> dimethoxyphenyl groups were introduced into the TBTQ skeleton. The Suzuki–Miyaura coupling of compound **10** with two different dimethoxyphenylboronic acids **11a** and **11b** was examined under various conditions. Finally, it was found that a combination of  $\text{Pd}(\text{OAc})_2$ – $\text{CsF}$ – $\text{SPhos}$  in dioxane at  $100^\circ\text{C}$  for 5 d was the optimum condition. Hence, compounds **4** and **5** were obtained in 97% and 89% yield, respectively, from tris-triflate **10** and the corresponding boronic acid. All of the synthesized compounds were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and mass spectrometry, and it was ensured that complete 3-fold coupling was achieved in both cases. Due to the magnetic shielding effect of the aryl rings introduced, the bay protons 5-H, 9-H, and 12-H of compounds **4** and **5** experienced a strong upfield shift (e.g.,  $\delta$  7.5  $\rightarrow$  5.7 for **5**),<sup>15</sup> while the positions of the bridgehead proton signals were slightly downfield shifted ( $\delta$  4.7  $\rightarrow$  5.0 for **5**) (Figures 2a and 2b). Interestingly, the  $^1\text{H}$  NMR spectra of



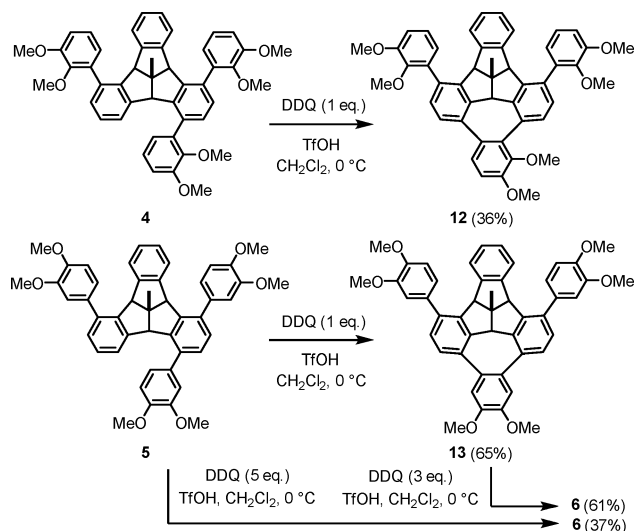
**Figure 2.** Stacked partial  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz, 20 °C) spectra of (a) tris-triflate **10**, (b) tris(3,4'-dimethoxyphenyl)-TBTQ **5**, (c) singly bridged V-shaped TBTQ **13**, and (d) triply bridged TBTQ **6**. Blue circles indicate  $^1\text{H}$  signals due to the inner bay protons that exhibit upfield shifts after arylation at C-1, C-4, and C-8 and disappear upon cycloheptatriene formation. Red squares indicate  $^1\text{H}$  signals due to the bridgehead protons before cycloheptatriene formation, which show downfield shifts after arylation. Green stars denote  $^1\text{H}$  signals due to the upfield shifted bridgehead protons after cycloheptatriene formation.

the tris(2',3'-dimethoxyphenyl)-TBTQ isomer **4** containing *o*-methoxy substituents showed extreme signal broadening but became well resolved at  $60^\circ\text{C}$ .<sup>15</sup> This observation is attributed to the hindered rotation about the newly formed aryl–aryl bonds due to steric interaction of the *o*-methoxy groups within the corresponding bays.

The cycloheptatriene ring formation of the tris(dimethoxyphenyl) derivatives **4** and **5** was tested under different conditions. Several oxidative systems including  $\text{FeCl}_3$ – $\text{MeNO}_2$ /CH<sub>2</sub>Cl<sub>2</sub>,<sup>16</sup>  $\text{AlCl}_3$ – $\text{Cu}(\text{OTf})_2$ /CS<sub>2</sub>,<sup>17</sup>  $\text{MoCl}_5$ /CH<sub>2</sub>Cl<sub>2</sub><sup>18</sup> and DDQ–TfOH/CH<sub>2</sub>Cl<sub>2</sub><sup>19</sup> were employed. With  $\text{FeCl}_3$  as the oxidant, only starting material was recovered. Use of  $\text{AlCl}_3$ – $\text{Cu}(\text{OTf})_2$  gave very messy product mixtures. Deeply colored, highly insoluble solids were obtained when  $\text{MoCl}_5$  was

employed. In the end, the DDQ–TfOH system turned out to be the most promising. Hence, the tris(2',3'-dimethoxyphenyl) **4** and tris(3',4'-dimethoxyphenyl) derivatives **5**, when treated with 1.0 equiv of DDQ, gave the V-shaped monocyclized products **12** and **13** in 36% and 65% yield, respectively (Scheme 2). The V-shaped structure of both compounds was

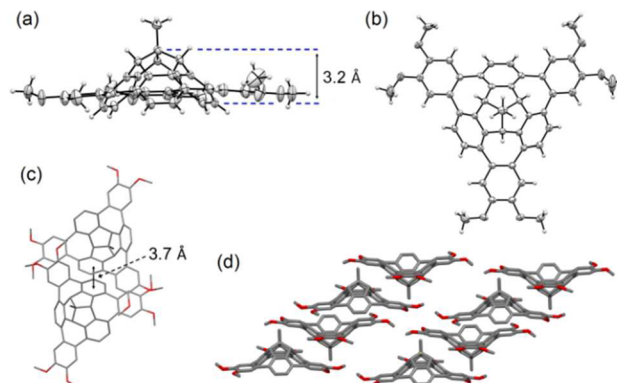
### Scheme 2. DDQ–TfOH-Promoted Oxidative Cycloheptatriene Ring-Formation Reactions



confirmed by 2D NMR experiments.<sup>15</sup> Upon cycloheptatriene formation, it was found that the <sup>1</sup>H NMR signal of the bridgehead protons belonging to the seven-membered rings experienced a significant shielding (e.g.,  $\delta$  5.0  $\rightarrow$  4.2 for compound **13**) induced by the 4,5-dimethoxy-1,2-phenylene bridge (Figure 2c). Despite numerous purification attempts, compound **12** was always contaminated with a small amount (10%) of the starting material **4**. Nevertheless, the identity of **12** could be unambiguously confirmed by various spectroscopic methods.<sup>15</sup> Notably, singly bridged isomers other than **12** and **13** were not found. The preference for the V-shaped isomers may be attributed to the fact that their formation involves electrophilic attack between the two most electron-rich biphenyl and *p*-terphenyl units in **4** and **5**. Furthermore, products **12** and **13**, having five aryl rings in conjugation, should be thermodynamically more stable than the unobserved regioisomers, which contain less such aryl rings. Further treatment of **12** with DDQ (3.0 equiv) failed to give the expected 3-fold cyclization product. It is believed that the elusive cyclization product of **12** would suffer from significant steric strain because of the presence of three methoxy groups at the bay positions. In stark contrast, under similar reaction conditions, compound **13** furnished the 3-fold cyclization product **6** in 61% yield. Moreover, we were unable to identify any doubly cyclized products. The structures of all compounds were again confirmed by NMR spectroscopy and mass spectrometry.<sup>15</sup> In particular, both the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the C<sub>3v</sub>-symmetrical product **6** were highly simplified as compared to those of the noncyclized **5** or monocyclized **13** precursors. Hence, the proton signals of 5-H, 9-H and 12-H disappeared, while the bridgehead protons were shifted upfield to  $\delta$  4.4 (Figure 2d). Direct treatment of compound **5** with excess DDQ (5.0 equiv) also gave compound **6** in comparable

yields (37%), but product purification was tedious because of the presence of many side products.

The wizard hat-shaped molecular structure of **6** was unambiguously confirmed by X-ray crystallography using a single crystal obtained from a pyridine solution of **6** by slow evaporation at 20 °C (Figure 3).<sup>15,20</sup> The concave shape was



**Figure 3.** Crystal structure of **6**: (a) side view with carbon atom positions shown as 50% probability ellipsoids; (b) top view; (c) convex–convex  $\pi$ – $\pi$  interactions in crystal packing of **6**; (d) molecular packing with hydrogen atoms and solvent molecules (pyridine) omitted for clarity.

generated by the three indan wings of the central TBTQ core, whereas the *o,p,o,p,o,p*-hexaphenylene rim, together with the three heptagons of negative curvature, formed the convex surface surrounding the TBTQ core. The depth of the hat<sup>21</sup> was found to be 3.2 Å, and the average dihedral angle between two indan planes was 111.6°. In the crystal packing, two neighboring molecules were packed with one molecule facing up and the other facing down. One of the aromatic rings of the original TBTQ core was found to stack in nearly parallel face-centered fashion with another TBTQ aromatic ring of the neighboring molecule, both via the convex faces. The intermolecular  $\pi$ – $\pi$  distance between the two rings is 3.7 Å. On the other hand, concave–concave  $\pi$ – $\pi$  stacking was not observed between any of the TBTQ aromatic rings and between any of the dimethoxy-substituted aromatic rings. The three axes crossing the central carbon and the centers of the outer peripheral indan C–C bonds meet each other at the central carbon at an angle of 78.0°. <sup>15</sup> Comparing these data with the parent hydrocarbon, 12D-methyltribenzotriquinacene,<sup>22</sup> in which the axes cross at 87.2° and the hat depth is 2.9 Å, reveals that the 3-fold bay-bridged TBTQ derivative **6** acquires an even more concave bowl structure. As for the *o,p,o,p,o,p*-hexaphenylene rim, the dihedral angle between two conjugated phenyl rings in **6** was found to be between 40–45°, whereas the corresponding dihedral angles of *o,p,o,p,o,p*-hexaphenylene, itself being a “des-neopentyl” analog of **6**, lie in the range of 40–75° according to theoretical calculations.<sup>23</sup> Hence the *o*- and *p*-phenylene rings are oriented in a significantly more coplanar manner in compound **6** as compared to the parent hydrocarbon.

Compound **6** is soluble in most organic solvents, resulting in an orange solution with weak purple fluorescence when irradiated with UV light. In chloroform, four absorption peaks at 238, 253, 273, and 300 nm could be resolved in the UV-absorption spectrum.<sup>15</sup> The low energy absorption onset was found to be 347 nm, reflecting a HOMO–LUMO gap of



3.57 eV. In the fluorescence spectrum, an emission maximum was observed at 380 nm upon excitation at 300 nm. The cyclic voltammogram of **6** in dichloromethane exhibits one quasi-reversible oxidation wave with half-wave oxidation potential of 1.09 V vs ferrocenium/ferrocene (first oxidation onset at 0.82 eV).<sup>15</sup> The HOMO and LUMO energy levels of **6** were estimated to be -5.92 and -2.35 eV, respectively.<sup>15</sup>

In summary, we reported the synthesis of an unprecedented wizard hat-shaped PAC **6** based on the TBTQ framework using a 3-fold Scholl-type cycloheptatriene formation reaction. The structural features, crystallographic packing modes, and optical and electronic properties of the TBTQ-PAC **6** were also examined. This new synthetic protocol, in principle, could also be applied to C<sub>3</sub>-symmetrical 1,5,9-triaryl-TBTQ compounds as starting materials.<sup>14b,c,24</sup> With the six methoxy groups available for further manipulations, extension of the curved aromatic surface to warped nanographenes such as **7** is underway in our laboratories.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05820.

Experimental details, NMR, X-ray, UV, and cyclic voltammetry data (PDF)  
X-ray data for **6** (CIF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*hfchow@cuhk.edu.hk

\*diemar.kuck@uni-bielefeld.de

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The work was supported by the UGC of HK (project no: AoE/P-03/08).

## ■ REFERENCES

- (1) (a) Hirsch, A.; Soi, A.; Karfunhel, H. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 766–768. (b) King, B. T.; Olmstead, M. M.; Baldrige, K. K.; Kumar, B.; Balch, A. L.; Gharamaleki, J. A. *Chem. Commun.* **2012**, *48*, 9882–9884. (c) Scott, L. T. *Chem. Soc. Rev.* **2015**, *44*, 6464–6471.
- (2) (a) Li, Z.; Liu, Z.; Sun, H.; Gao, C. *Chem. Rev.* **2015**, *115*, 7046–7117. (b) Narita, A.; Wang, X.-Y.; Feng, X.; Müllen, K. *Chem. Soc. Rev.* **2015**, *44*, 6616–6643. (c) Segawa, Y.; Yagi, A.; Matsui, K.; Itami, K. *Angew. Chem., Int. Ed.* **2016**, *55*, 5136–5158.
- (3) (a) Yamamoto, K.; Saitho, Y.; Iwaki, D.; Ooka, T. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1173–1174. (b) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868–4884. (c) Wu, Y.-T.; Siegel, J. S. *Chem. Rev.* **2006**, *106*, 4843–4867. (d) Bharat; Bhola, R.; Bally, T.; Valente, A.; Cyrański, M. K.; Dobrzycki, L.; Spain, S. M.; Rempala, P.; Chin, M. R.; King, B. T. *Angew. Chem., Int. Ed.* **2010**, *49*, 399–402. (e) Luo, J.; Xu, X.; Mao, R.; Miao, Q. *J. Am. Chem. Soc.* **2012**, *134*, 13796–13803. (f) Feng, C.-N.; Kuo, M.-Y.; Wu, Y.-T. *Angew. Chem., Int. Ed.* **2013**, *52*, 7791–7794. (g) Kawasumi, K.; Zhang, Q.; Segawa, Y.; Scott, L. T.; Itami, K. *Nat. Chem.* **2013**, *5*, 739–744. (h) Sakamoto, Y.; Suzuki, T. *J. Am. Chem. Soc.* **2013**, *135*, 14074–14077. (i) Miller, R. W.; Duncan, A. K.; Schneebeli, S. T.; Gray, D. L.; Whalley, A. C. *Chem. - Eur. J.* **2014**, *20*, 3705–3711. (j) Cheung, K. Y.; Xu, X.; Miao, Q. *J. Am. Chem. Soc.* **2015**, *137*, 3910–3914. (k) Kato, K.; Segawa, Y.; Scott, L. T.; Itami, K. *Chem. - Asian J.* **2015**, *10*, 1635–1639.
- (4) (a) Pascal, R. A.; McMillan, W. D.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 5652–5653. (b) Lu, J.; Ho, D. M.; Vogelaar, N. J.; Kraml, C. M.; Pascal, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 11168–11169. (c) Collins, S. K.; Grandbois, A.; Vachon, M. P.; Côté, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 2923–2926. (d) Xiao, J.; Duong, H. M.; Liu, Y.; Shi, W.; Ji, L.; Li, G.; Li, S.; Liu, X.-W.; Ma, J.; Wudl, F.; Zhang, Q. *Angew. Chem., Int. Ed.* **2012**, *51*, 6094–6098. (e) Arslan, H.; Uribe-Romo, F. J.; Smith, B. J.; Dichtel, W. R. *Chem. Sci.* **2013**, *4*, 3973–3978. (f) Pradhan, A.; Dechambenoit, P.; Bock, H.; Durola, F. *J. Org. Chem.* **2013**, *78*, 2266–2274. (g) Fujikawa, T.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2015**, *137*, 7763–7768. (h) Kashiwara, H.; Asada, T.; Kamikawa, K. *Chem. - Eur. J.* **2015**, *21*, 6523–6527.
- (5) Scholl, R.; Mansfeld, J. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1734–1746.
- (6) Grzybowski, M.; Skonieczny, K.; Butenschön, H.; Gryko, D. T. *Angew. Chem., Int. Ed.* **2013**, *52*, 9900–9930.
- (7) (a) Iyer, V. S.; Wehmeier, M.; Brand, J. D.; Keegstra, M. A.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1604–1607. (b) Simpson, C. D.; Brand, J. D.; Berresheim, A. J.; Przybilla, L.; Räder, H. J.; Müllen, K. *Chem. - Eur. J.* **2002**, *8*, 1424–1429. (c) Yang, X.; Dou, X.; Rouhanipour, A.; Zhi, L.; Räder, H. J.; Müllen, K. *J. Am. Chem. Soc.* **2008**, *130*, 4216–4217. (d) Vo, T. H.; Shekhirev, M.; Kunkel, D. A.; Orange, F.; Guinel, M. J. F.; Enders, A.; Sinitskii, A. *Chem. Commun.* **2014**, *50*, 4172–4174. (e) Lorbach, D.; Keerthi, A.; Figueira-Duarte, T. M.; Baumgarten, M.; Wagner, M.; Müllen, K. *Angew. Chem., Int. Ed.* **2016**, *55*, 418–421.
- (8) (a) Rempala, P.; Kroulík, J.; King, B. T. *J. Am. Chem. Soc.* **2004**, *126*, 15002–15003. (b) Rempala, P.; Kroulík, J.; King, B. T. *J. Org. Chem.* **2006**, *71*, 5067–5081. (c) King, B. T.; Kroulík, J.; Robertson, C. R.; Rempala, P.; Hilton, C. L.; Korinek, J. D.; Gortari, L. M. *J. Org. Chem.* **2007**, *72*, 2279–2288. (d) Ormsby, J. L.; Black, T. D.; Hilton, C. L.; Bharat; King, B. T. *Tetrahedron* **2008**, *64*, 11370–11378.
- (9) (a) Tellenbröcker, J.; Kuck, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 919–922. (b) Tellenbröcker, J.; Kuck, D. *Eur. J. Org. Chem.* **2001**, *2001*, 1483–1489. (c) Kuck, D. *Chem. Rev.* **2006**, *106*, 4885–4925.
- (10) Mughal, E. U.; Kuck, D. *Chem. Commun.* **2012**, *48*, 8880–8882.
- (11) Mughal, E. U.; Neumann, B.; Stammmer, H.-G.; Kuck, D. *Eur. J. Org. Chem.* **2014**, *2014*, 7469–7480.
- (12) An, P.; Chow, H.-F.; Kuck, D. *Synlett* **2016**, *27*, 1255–1261.
- (13) Kirchwehm, Y.; Damme, A.; Kupfer, T.; Braunschweig, H.; Krüger, A. *Chem. Commun.* **2012**, *48*, 1502–1504.
- (14) (a) Kuck, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 508–509. (b) Xu, W.-R.; Chow, H.-F.; Cao, X.-P.; Kuck, D. *J. Org. Chem.* **2014**, *79*, 9335–9346. (c) Xu, W.-R.; Chow, H.-F.; Cao, X.-P.; Kuck, D. *J. Org. Chem.* **2015**, *80*, 4221–4222.
- (15) See the Supporting Information for details.
- (16) Feng, X.; Wu, J.; Enkelmann, V.; Müllen, K. *Org. Lett.* **2006**, *8*, 1145–1148.
- (17) Dötz, F.; Brand, J. D.; Ito, S.; Gherghel, L.; Müllen, K. *J. Am. Chem. Soc.* **2000**, *122*, 7707–7717.
- (18) Kramer, B.; Averhoff, A.; Waldvogel, S. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2981–2982.
- (19) Zhai, L.; Shukla, R.; Rathore, R. *Org. Lett.* **2009**, *11*, 3474–3477.
- (20) CCDC-1474467 contains the supplementary crystallographic data for **6**.
- (21) The hat depth is defined as the distance of the central quaternary carbon atom to the plane defined by the three midpoints of the C5–C6, C11–C12, and C17–C18 bonds of compound **6**.
- (22) Brandenburg, J. G.; Grimme, S.; Jones, P. G.; Markopoulos, G.; Hopf, H.; Cyrański, M. K.; Kuck, D. *Chem. - Eur. J.* **2013**, *19*, 9930–9938.
- (23) Fujioka, Y. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3494–3506.
- (24) Markopoulos, G.; Henneicke, L.; Shen, J.; Okamoto, Y.; Jones, P. G.; Hopf, H. *Angew. Chem., Int. Ed.* **2012**, *51*, 12884–12887.