



Regio-defined multi-hydroxylation of Dibenzo[*g,p*]chrysene

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ABSTRACT

Regioselective direct tetra-bromination of dibenzo[*g,p*]chrysene (DBC) is described, involving the synthesis of multi-hydroxyl DBC derivatives. Addition of 16 equiv Br₂ to a suspension of DBC in CH₂Cl₂ enables to singly construct a 2,7,10,15-tetrabromo-DBC. A lithium-bromine exchange event leads the corresponding silyl molecule, and the following oxidation formed a tetra-hydroxyl derivative. Its isomeric tetra-hydroxyl DBC as well as more congested octa-hydroxyl DBC were also singly constructed. These straightforward and simple synthetic routes would provide a general entry for new DBC materials.

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Introduction

Dibenzo[*g,p*]chrysene core, shown in Fig. 1, has attracted much interest, because it constitutes a unique class of polycyclic aromatic hydrocarbons (PAHs) [1a–c,2a,b,3]. It originally features a helically twisted π -conjugation [4a,b], which is expected to apply to a thin-film transistor as a hole transporting material [5a–c], and an organic light-emitting diode as an emissive material [6]. Chemists have tried to synthetically functionalize the fused-ring core to set up molecular diversity for tuning properties, which can enable us to make new materials [7a–e]. For example, as one of those materials, there is a polymer assembly in which we chemists desire to deploy a dibenzo[*g,p*]chrysene (DBC): photophysical and electronic properties such as high quantum yields, and long excited lifetime, and capacity for resisting heat are supposed to advance much more [8]. Despite the relevant possibilities of the DBC, direct and selective functionalization of the DBC core has not been well explored so far. Even regio-defined introduction of fundamental substituents such as hydroxyl groups and bromine atoms into the core has been quite a problem [9]. Actually, synthesis of multi-substituted DBCs with precision of stereo-chemistry requires tedious synthetic process and laborious separation between isomers [10a,b].

Herein we report stereo-defined syntheses of DBC derivatives tethered hydroxyl groups those are **1** in 2,7,10,15-positions, **2** in

3,6,11,14-positions, and **3** in 2,3,6,7,10,11,14,15-positions (Fig. 1). Most patents about DBCs focus on attachment of multiple hydroxyl groups into the cores toward the various polymer syntheses; however, the regio-selective attachments are problematic [9]. This drove us to singly construct isomeric DBCs tethered hydroxyl groups. Synthesis of **1** was based on direct and regio-selective bromination of DBC. Syntheses of **2** and **3** were derived from 2,7-dimethoxy fluorenone.

We started investigation with a large scale preparation of DBC (Scheme 1), because commercially available DBC was too expensive (for our group) [11]. We made use of the patent information, and altered the experimental procedure to fit our hand [12a,b]. Dimerization of 9-fluorenone of 80 g proceeded when triethyl phosphite was used as solvent at 175 °C, and the successive hydrolysis gave the corresponding pinacol-type adduct. Pinacol rearrangement of the diol in refluxing methanol yielded the spiro compound in 65%, and the following Wagner-Meerwein rearrangement formed DBC skeleton in 82% yield. We confirmed reproducibility to repeat these experiments 20 times, and prepared about 500 g of DBC.

The adequate amounts of DBC enabled us to have many early experiments for finding good reaction condition of regio-selective bromination of DBC core; finally, usage of Br₂ was found to singly yield **4** that has four bromines (Scheme 2). Upon addition of 16 equivalent bromine to a suspension of DBC in CH₂Cl₂ solvents, to our surprise, a perfectly regio-selective tetra-bromination occurred within 30 min. Even in the crude state, TLC and ¹H NMR spectrum indicated that the product **4** was solely produced in pure form.

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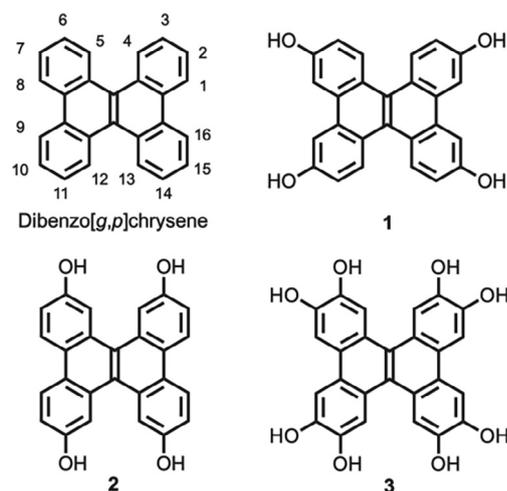
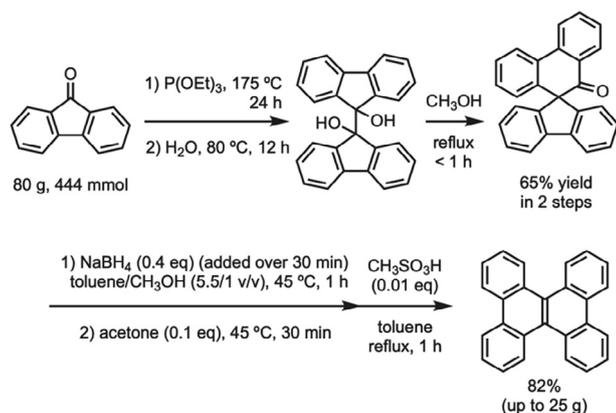
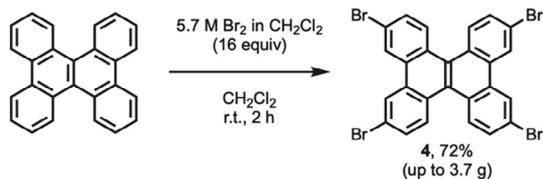


Fig. 1. Dibenzo[*g,p*]chrysene, **1**, **2**, and **3**.

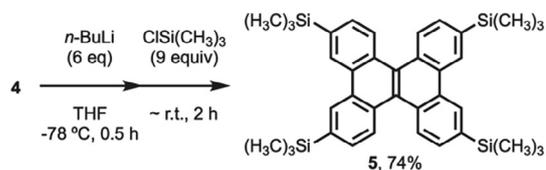


Scheme 1. Synthesis of dibenzo[*g,p*]chrysene through dimerization reaction of fluorenone.



Scheme 2. Regio-selective tetra-bromination of dibenzo[*g,p*]chrysene to form **4**.

When usage amounts of bromine decreased to 12 equiv, the reaction completed barely in 24 h. We also attempted to use 8 and 4.8 equiv of bromines, and observed incomplete bromination along with unpleasant mixtures in TLC monitoring and messy peaks of ¹H NMR charts. The single operation of recrystallization from toluene yielded **4** in 72% although **4** dissolved sparingly [13]. At this point the positions of four bromines were unidentified, so we tried to make a single crystal for X-ray analysis; however, a lot of efforts preparing the crystal was unsuccessful. Thus, we mapped out our target molecule, the molecule is tetra-silyl **5** (Scheme 3). Although the solubility of **4** in THF solvent was terribly low, we envisaged that multiple lithiation would proceed [14]: to a suspension of **4** in THF at -78 °C was added *n*-BuLi (6 equiv), which was subjected to reaction with chlorotrimethylsilane (TMSCl, 9 equiv). In spite of the suspension state, high-yielding transformation was achieved in 74% to give tetra-TMS **5**. The molecular structure of **5** was determined by crystallographic analysis (Fig. 2), which disclosed the arrangement of four substituents in



Scheme 3. Synthesis of **5**.

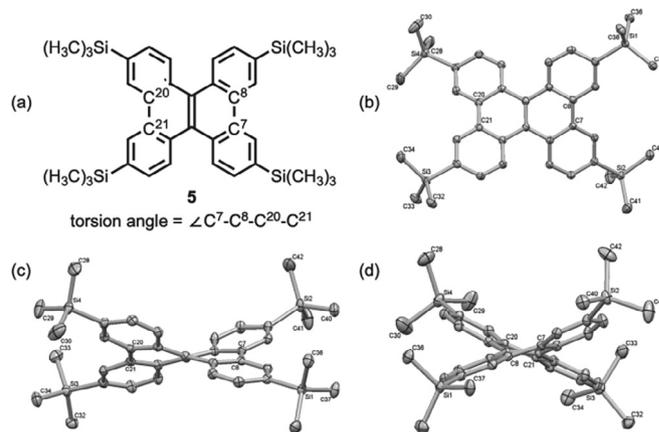
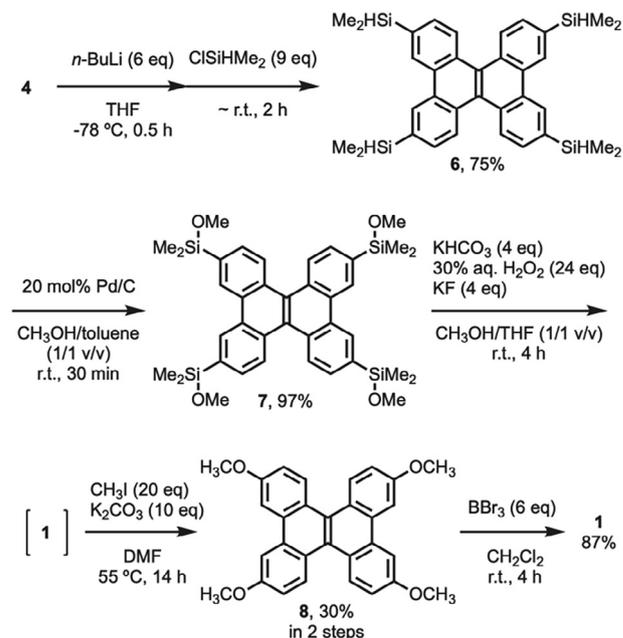


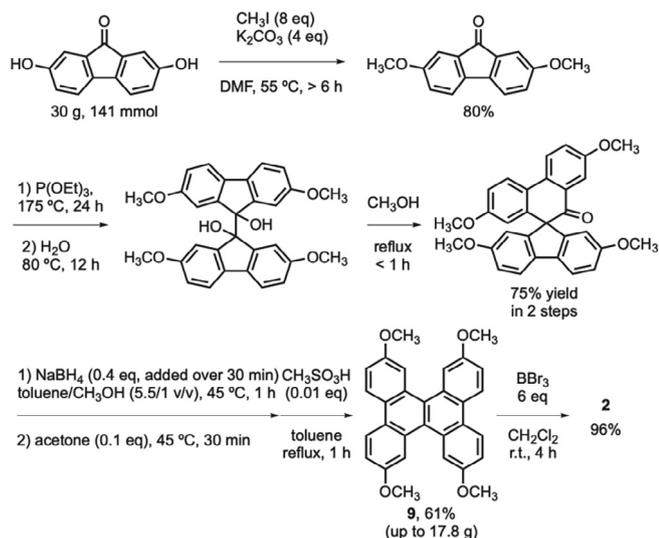
Fig. 2. Molecular and packing structures with ORTEP drawing of **5** with thermal ellipsoids at the 50% probability level; (a) torsion angles determined by the four carbon atoms of C⁷, C⁸, C²⁰, and C²¹; (b) top view; (c) side view from a fjord-area region with a description of the torsion angle 41.14°; (d) side view from a bay-area region. The hydrogen atoms are omitted for clarity.

2,7,10,15-positions as illustrated in Scheme 2 [15,16]. And the characteristic twisted structure, to our surprise, was displayed with the torsion angle of 41.1° that was larger than the maximum value of 37.3° reported by Nakamura et al. [10b] [17]. Indeed, judging from the illustrations of part (c) and (d) in Fig. 2, the pi-conjugated **5** obviously and actively bent.

With the success in preparing the tetra-silyl **5**, we prepared the structurally similar tetra-hydrodimethylsilyl **6** in 75% yield because we anticipated that Fleming-Tamao oxidation of **6** is effective for synthesis of **1** (Scheme 4) [18a,b]. Indeed, it looked so, but **6**



Scheme 4. Synthetic route to **1** via **6**, **7**, and **8**.

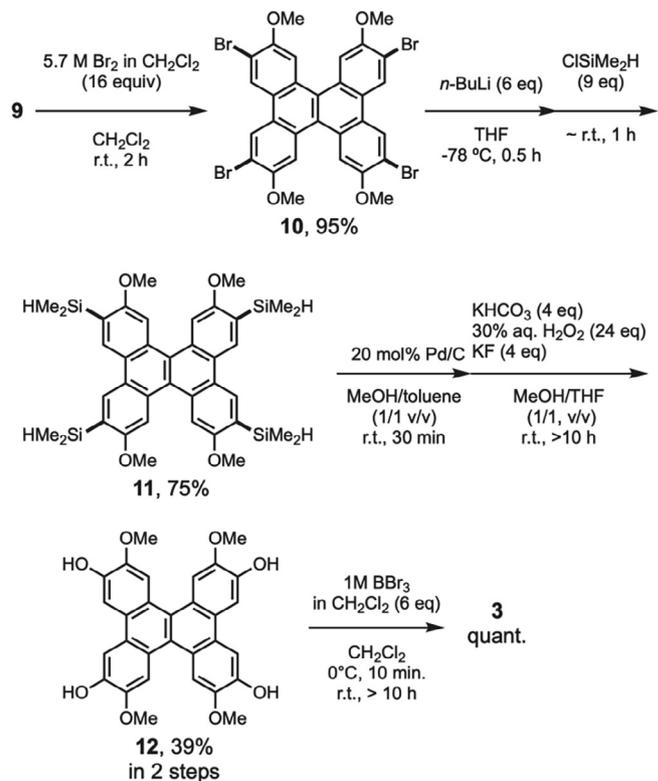
Scheme 5. Synthesis of **2** via **9**.

didn't have enough reactivity to complete the oxidation process. Hence, **6** was converted into the highly reactive and somewhat unstable tetra-methoxysilyl **7** in 97% yield [19]. Actually, the oxidation of **7** quickly proceeded in TLC monitoring, and obviously produced **1** in the crude state; however, annoying impurities prevented us from purifying **1**. Thus, the resultant crude products were successively subjected to tetra-methylation, and **8** was obtained in pure form in 30%. Finally, clean demethylation of **8** by BBr_3 was completed, giving desired **1** in 87%.

We next focused on the synthesis of **2** (Scheme 5): in the same way of constructing the DBC skeleton, dimerization of 2,7-dimethoxy fluorenone of 80 g proceeded when triethyl phosphite was used as solvent at 175 °C, and the successive hydrolysis gave the corresponding pinacol-type adduct. Pinacol rearrangement of the diol in refluxing methanol yielded the spiro compound in 75%, and the following Wagner-Meerwein rearrangement formed DBC skeleton in 61% yield. We repeated these experiments 7 times, and prepared about 170 g of **9**. Finally, **9** undertook smooth demethylation by means of BBr_3 , giving **2** in 96% yield.

Through the course of pursuing the synthesis of tetrol **1** and **2**, the structure of octol **3** intrigued us. We have explored possibility of singly shaping **3** that has eight phenolic hydroxyl groups in the same positions as **1** and **2** (Scheme 6). Luckily, the starting **9** cleanly undertook a selective bromination at 2,7,10,15-positions in 95% yield. The resultant **10** accepted tetra-silylation to yield **11** in 75%. The following methoxysilylation for being much more reactive toward Fleming-Tamao oxidation successfully led to **12** that has four methoxy and four hydroxyl groups. Finally, clean demethylation by BBr_3 was carried out to give desired **3** as blue crystals in quantitative yield.

In summary, regio-defined multiple introduction of hydroxyl groups into a DBC core was successfully demonstrated. Key to these single constructions were three: One, smooth dimerization reactions of 9-fluorenone analogues readily prepared DBC skeletons in 18–25 g of laboratory-scale. Two, DBC undertook direct tetra-bromination in perfectly regio-selective manner. Three, the four bromines tethered DBC were all together tolerable to Fleming-Tamao oxidation reactions. These three simple findings enable us to separately make new multiple hydroxyl DBC in pure form. This demonstration would be good opportunity for understanding reactivity of DBC core and opening the door of creating new functional organic materials anchored to the DBC. Application to polymer assembly materials is ongoing and will be reported in due course.

Scheme 6. Synthetic route to **3** via **10**, **11**, and **12**.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.tetlet.2020.152033>.

References

- [1] a) E. Clar, *Polycyclic Aromatic Hydrocarbons*, vol. Academic Press, London, I,II, 1964;
b) R.G. Harvey, *Polycyclic Aromatic Hydrocarbons*, Wiley, New York, 1997;
c) H. Hopf, *Classics in Hydrocarbon Chemistry*, Wiley-VCH, Weinheim, Germany, 2000.
- [2] a) J.C. Fetzer, *Polycyclic Aromat. Compd.* 27 (2007) 143–162;
b) R.A. Pascal Jr., *Chem. Rev.* 106 (2006) 4809–4819.
- [3] S. Kumar, S.K. Varshney, *Mol. Cryst. Liq. Cryst.* 378 (2002) 59–64.
- [4] a) F.H. Herbststein, *Acta Crystallogr. B* 35 (1979) 1661;
b) H. Tsuji, Y. Ueda, L. Ilies, E. Nakamura, *J. Am. Chem. Soc.* 132 (2010) 11853–11855.
- [5] a) S. Wang, P. Yang, K. Chang, W. Lv, B. Mi, J. Song, X. Zhao, Z. Gao, *Org. Electron.* 74 (2019) 269–275;
b) T. Mori, K. Fujita, M. Kimura, *J. Photopolym. Sci. Technol.* 23 (2010) 317–322;

- c) R. Chaudhuri, M.-Y. Hsu, C.-W. Li, C.-I. Wang, C.-J. Chen, C.-K. Lai, L.-Y. Chen, S.-H. Liu, C.-C. Wu, R.S. Liu, *Org. Lett.* **10** (2008) 3053–3056.
- [6] S. Tokito, K. Noda, H. Fujikawa, Y. Taga, M. Kimura, K. Shimada, *App. Phys. Lett.* **77** (2000) 160–162.
- [7] a) C.L. Eversloh, Z. Liu, B. Müller, M. Stangl, C. Li, K. Müllen, *Org. Lett.* **13** (2011) 5528–5531;
b) T. Hatakeyama, S. Hashimoto, S. Seki, M. Nakamura, *J. Am. Chem. Soc.* **133** (2011) 18614–18617;
c) Xiao, S.; Kang, S. J.; Wu, Y.; Ahn, S.; Kim, J. B.; Loo, Y.-L.; Siegrist, T. Steigerwald, M. L.; Li, H.; Nuckolls, C. *Chem. Sci.* **2013**, *4*, 20182–20183;
d) K. Nakamura, S. Furumi, M. Takeuchi, T. Shibuya, K. Tanaka, *J. Am. Chem. Soc.* **136** (2014) 5555–5558;
e) Sakamaki, K.; Kumano, D.; Yashima, E. *Angew. Chem. Int. Ed.* **2015**, *54*, 5404–5407
- [8] S. Yamaguchi, T.M. Swager, *J. Am. Chem. Soc.* **123** (2001) 12087–12088.
- [9] a) Makinoshima, T.; Echigo, M. *PCT Int. Appl.* (2015), WO 2015170736 A1 20151112; b) Kato, H.; Takatori, M. *Jpn. Kokai Tokkyo Koho* (2014), JP 2014152164 A 20140825; c) Kato, H.; Takatori, M. *Jpn. Kokai Tokkyo Koho* (2013), JP 2013227307 A 20131107; c) Ohta, K. *Jpn. Kokai Tokkyo Koho* (2016), JP 2016-125007 A 20160711.
- [10] a) N. Suzuki, T. Fujita, J. Ichikawa, *Org. Lett.* **17** (2015) 4984–4987;
b) Y. Ueda, H. Tsuji, H. Tanaka, E. Nakamura, *Chem. Asia. J.* (2014) 1623–1628.
- [11] Commercially available dibenzo[g,p]chrysene (CAS# 191-68-4) in Tokyo Chemical Industry Co., Ltd. is 1 g at the maximum amount that costs us ¥ 44,000 (without tax).
- [12] a) H. Yamada, M. Uchida, *Jpn. Kokai Tokkyo Koho JP* (2011) 2011–6397;
b) M. Takatori, *Jpn. Kokai Tokkyo Koho JP* (2016) 2016–193873.
- [13] 350 mL of refluxing toluene dissolved 1 g of **4**, which was followed by removal of 140 mL of toluene to start crystallization.
- [14] We already experienced the smooth lithiation of pyrene (C₁₆H₁₀) even in the THF suspension state: see, A. H. Sato, M. Maeda, S. Mihara, T. Iwasawa, *Tetrahedron Lett.* **2011**, *52*, 6284–6287
- [15] The single crystal of **5** was prepared by slow evaporation of CH₃CN (4 mL) solution of the sample (5 mg); CCDC-1989053 (for **5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Orthorhombic, space group P212121, colorless, a = 11.0789(1) Å, b = 16.3902(1) Å, c = 21.0841(1) Å, α = 90°, β = 90°, γ = 90°, V = 3828.56(5) Å³, Z = 4, T = 293 K, d_{calcd.} = 1.071 g cm⁻³, μ(Mo-Kα) = 1.601 mm⁻¹, R₁ = 0.0259, wR₂ = 0.0714, GOF = 1.029.
- [16] Nakamura and co-workers, in ref. 10 b), reported the frontier molecular orbital coefficients are almost equal over all carbon atoms of the non-substituted DBC by means of CV measurements and DFT calculations.
- [17] At this time, the reasonable reason why the novel molecule **5** has the large torsion angle is not clear. The four silyl atoms in **5** might influence the angle.
- [18] a) K. Tamao, M. Akita, M. Kumada, *Organometallics* **2** (1983) 1694–1696;
b) I. Fleming, R. Henning, H. Plaut, *J. Chem. Soc., Chem. Commun.* (1984) 29–31.
- [19] E.J. Rayment, N. Summerhill, E.A. Anderson, *J. Org. Chem.* **77** (2012) 7052–7060.