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Straightforward synthetic routes to well-soluble and regio-defined dibenzo[*g*,*p*]chrysene derivatives

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ABSTRACT

A straightforward route to a well-soluble dibenzo[*g*, *p*]chrysene (DBC) scaffold is described. The scaffold is 2,7-dibromo-10,15-dibutyl DBC, in which two butyl groups work as a solubilizing agent and two bromines play a role of changeable tags. This solution-processable DBC enabled diversity-oriented approaches for synthesis of solubilizing DBC derivatives: actually, one of the two bromines selectively undertook the first transformation, and the other bromine was subjected to the second substitution reaction. Thus, the new DBC platform provides a general entry for creation of new polycyclic aromatic hydrocarbons.

Regio-defined arrangement of substituents at the periphery of polycyclic aromatic hydrocarbons (PAHs) is synthetically important technique, because of the possibility to manipulate spectroscopic, optoelectronic, and photophysical properties [1–3]. We chemists have functionalized the fused-ring cores to set up molecular diversity, which enables us to make new organic materials [4,5]. On the other hand, PAHs are typically insoluble in organic solvents and generally symmetrical shapes: hence, chemical modifications with high precision are basically embarrassing work [6].

Among such types of PAHs, dibenzo[*g*,*p*]chrysene (DBC) is one of the most attractive fused rings [7]. Because its originally twisted π -conjugations influence molecular packing and the resultant solid state property such as carrier transportation [8,9]. In addition, fine tunings in structure of DBC skeleton allow manipulation of the photophysical and electronic attributes such as good hole mobilities, high quantum yields, and long excited state lifetime [10,11]. However, low solubility of DBC hampers much more flexible transformations. Even if the steric congestion lead by peripheral hydrogen atom at 4,5,12,13-positions makes the core twisted with somewhat of a solubility, they sparingly dissolve in organic solvents. Indeed, Fan group excellently synthesized 3,6,11,14-tetrabromo-DBC as a molecular scaffold, but it was practically insoluble and inconvenient for further transformation [12].

Herein we report synthesis of a well-soluble and tunable DBC platform molecule **1**, namely 2,7-dibromo-10,15-dibutyldibenzo[*g*,*p*]chrysene (Fig. 1). The platform features a solution processable molecule because of two butyl groups as solubilizing agents and a diversity-oriented scaffold owing to two bromine sites as changeable tags. We anticipated that various kinds of multiple substituted DBC analogues are created from **1**.

At the outset of this study, we prepared sufficient amounts of DBC, around 500 g, according to our previous report because commercially available DBC was too expensive (for our group) [13,14]. We envisaged that DBC might undertake Friedel-Crafts alkylation reactions, and attempted reactions between DBC and *tert*-BuCl/isoPrCl in the presence of $FeCl_3$ and $AlCl_3$. However, products were not singly produced presumably due to over-reactions those are typical side-reactions in such Friedel-Crafts type-transformation. Then, butyryl chloride was used as an electrophilic partner; to our surprise, regio-selectively 2,7-disubstituted DBC **2** was isolated in 77% yield among three possible isomers of 2,7-, 2,10-, 2,15-diketones (Scheme 1) [15]. ^{13}C NMR spectrum of **2** gave 18 peaks of 2,7-diketones, although 2,10-, 2,15-diketones should show 17 peaks [16]. Thus, the following deoxygenation reaction of **2** by $AlCl_3$ and $NaBH_4$ formed dibutyl compound **3** in 78% (up to 2.7 g) [17], and the final selective dibromination of **3** at 10- and 15-positions proceeded in 78% yield (up to 2.3 g) to give **1**. The solubility of **3** was definitely improved because 1 mmol of **3** dissolved into 3 mL of CH_2Cl_2 but 1 mmol of unsubstituted DBC barely dissolved into 100 mL of CH_2Cl_2. Although we tried to prepare the single

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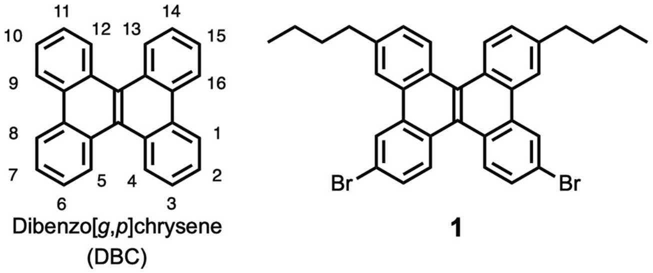
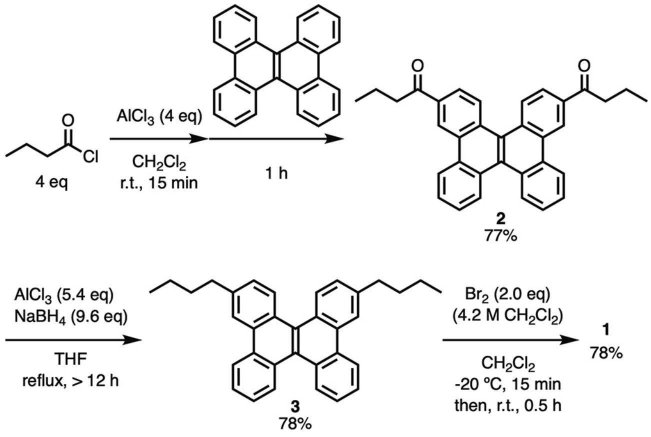


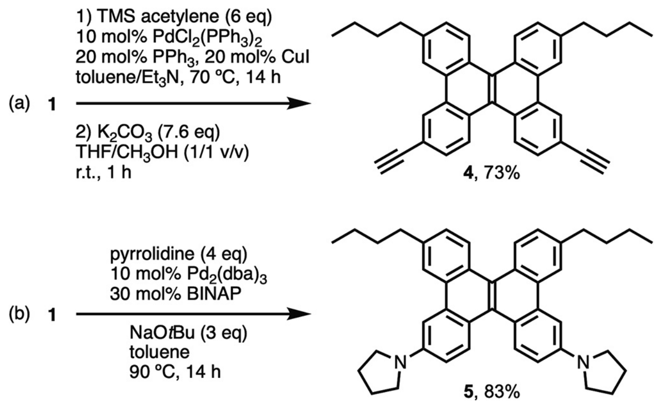
Fig. 1. Dibenzo[*g*,*p*]chrysene (DBC), and **1**.



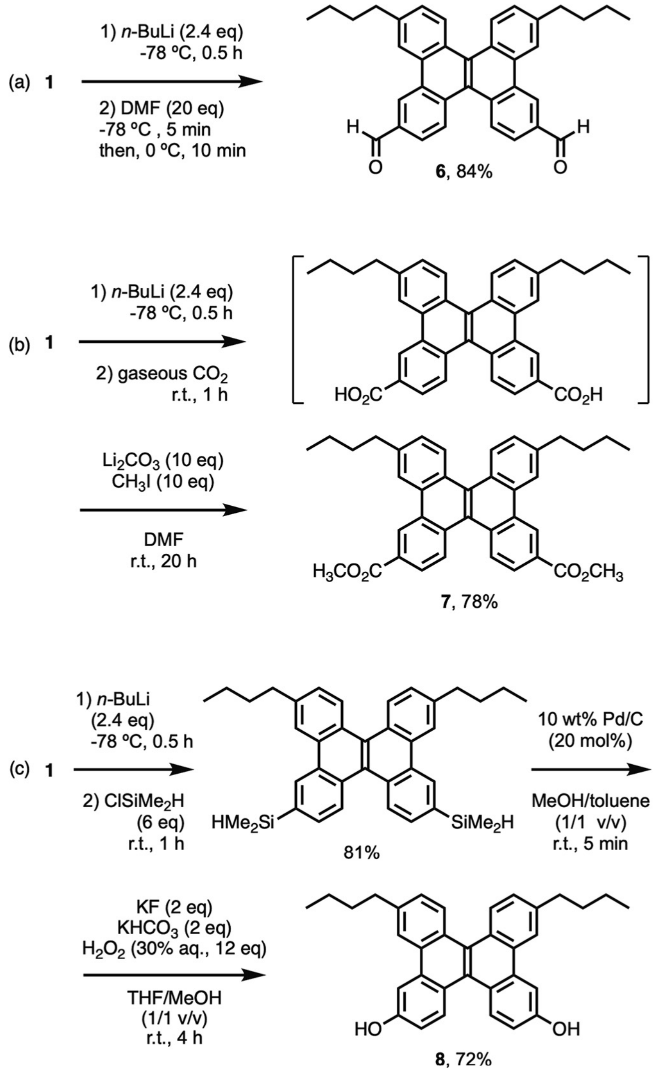
Scheme 1. Three step synthesis of **1** from dibenzo[*g*,*p*]chrysene *via* **2** and **3**.

crystal of **1** for the crystallographic analysis, but it was unsuccessful at this stage [18].

With a viable protocol of solution-processable **1** in hand, we demonstrated two kinds of substitution reactions at the two bromine sites. First, conventional palladium-catalyzed cross-coupling reactions were performed (Scheme 2). **1** undertook Sonogashira reaction to afford bis-terminal alkyne **4** in 73% yield (part (a)), [19] and Buchwald-Hartwig amination to yield bis-pyrrolidine **5** in 83% (part (b)). Second, lithium–halogen exchange of dibromide **1** was carried out (Scheme 3) [20]. The corresponding dianion was produced in THF at −78 °C, and transformed into bis-aldehyde **6** in 84% yield (part (a)). For part (b), the bis-carboxylic acid was prepared through CO_2 bubbling although isolation of the acid in pure form was difficult. The acid was consecutively transformed into dimethyl ester **7** in 78% yield. For Fleming-Tamao oxidation protocol in part (c), three steps transformations were required for smooth production of **8**. The silylation reaction *via* lithium–halogen exchange occurred in 81%, which was followed by the methoxy-silylation and oxidation to give green-colored solid **8** in 72% yield [21]. To our surprise, bis-phenol **8** was purified by silica-gel column chromatography without any difficulties such as terrible adsorption onto the gel.

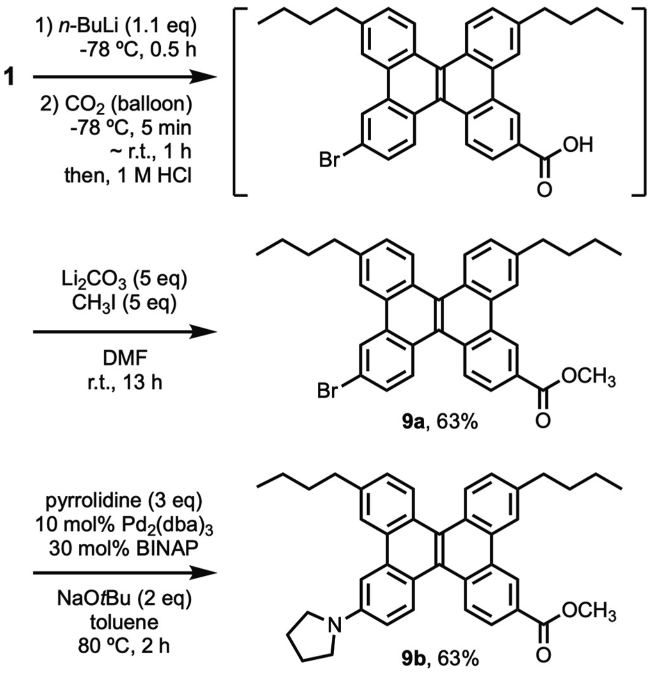


Scheme 2. Synthesis of (a) **4** and (b) **5** through cross-coupling reactions.

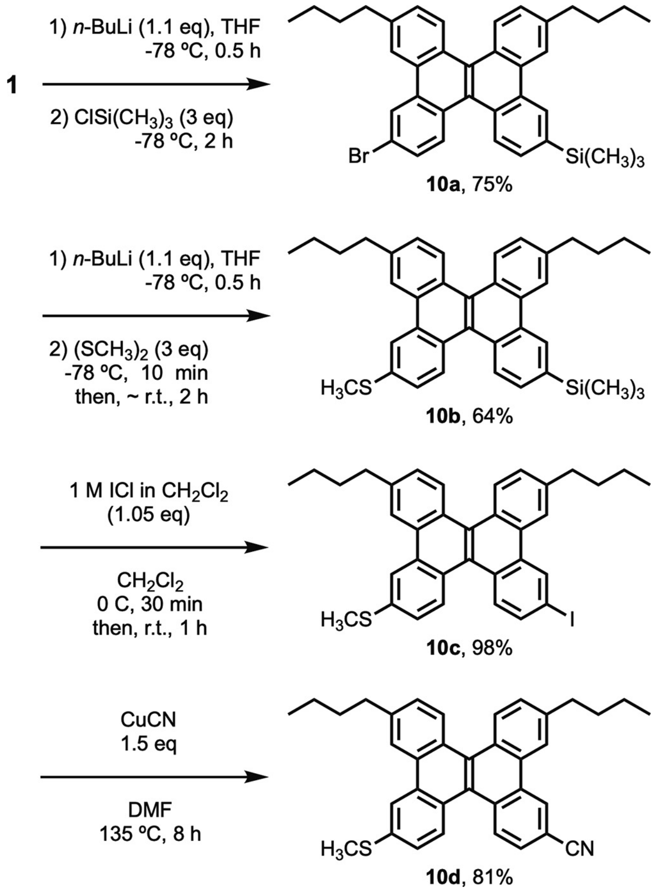


Scheme 3. Synthesis of (a) **6**, (b) **7**, and (c) **8** through lithium–halogen exchange reactions.

Does **1** undertake the selective activation in one side bromine? **1** was subjected to a mono-lithiation condition (Scheme 4). Fortunately, the symmetric **1** was subjected to the single lithiation event and successive reaction with gaseous CO_2, which was followed by methylation to afford dissymmetric ester **9a** in 63% yield. And the other bromine site was successfully substituted with pyrrolidine through Buchwald-Hartwig amination, giving **9b** in 63% yield. The structure of **9b** having electronic donor and acceptor moieties can be a candidate for materials of "push–pull-type" dyes [22]. The induction of this type of dissymmetry is applicable to preparation of compound **10a** that masks one of the two bromines in **1**: the trimethylsilyl (TMS) moiety in **10a** is equivalent to iodine synthon (Scheme 5). Although CuCN-mediated cyanation of bromine sites in **1** was not observed in mild condition, the trimethylsilyl protective group (TMS) in **10a** proved to be a solution to the problem. The *mono*-lithiation of **1** and the following silylation afforded **10a** in 75% yield. The mono-bromide **10a** was transformed into methyl



Scheme 4. Synthesis of mono-bromide **9a** and electronic push–pull-type **9b**.

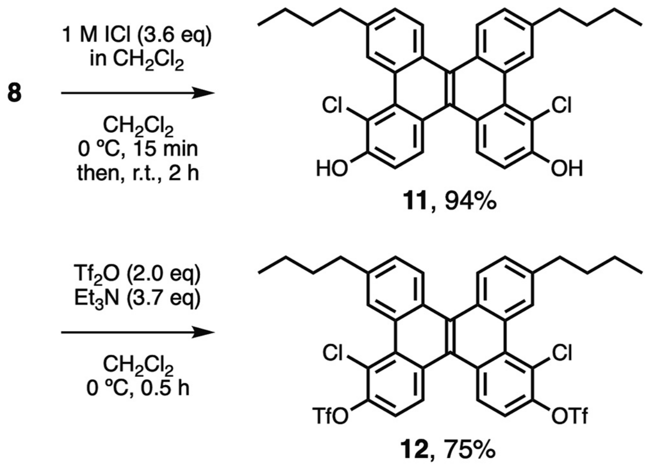


Scheme 5. Synthesis of masked bromide **10a**, and sulfide **10b**, and iodide **10c**, and nitrile **10d**.

sulfide **10b**, and followed by de-silylative iodination to give iodide **10c** in 98% yield [23]. **10c** was amenable to Rosenmund-von Braun cyanation at 135 °C, practically giving nitrile **10d** in 81% yield [24,25]. Thus, TMS-substituted **10a** is also appreciated as a scaffold for synthesizing diverse dissymmetric DBC derivatives.

Lastly, we again intensively tried to determine the above-mentioned DBC structures by crystallographic analysis; thus, this led us to find the regio-specific chlorination and to establish compounds **11** and **12** (Scheme 6). Upon addition of iodine mono-chloride (ICl) to **8** in CH_2Cl_2, regio-specific chlorination reactions occurred doubly at *ortho*-positions adjacent to hydroxyl groups, giving **11** in 94% yield. The reaction of **11** with trifluoromethanesulfonic anhydride (Tf_2O) was carried out to form **12** in 75% yield. To our delight, after many trials, slow evaporation of the acetone solution of **12** successfully made single crystals. The molecular structure of **12** was crystallographically ascertained (Fig. 2), which clearly disclosed the arrangement of two chlorines, two triflates, and two butyl groups **12** as illustrated in Scheme 6 [26] And the characteristic twisted structure with its torsion angle of 47° is also revealed, and this large value was out of range from 28.6° to 37.3° that was reported by Nakamura and co-workers [7a]. As a supplement, **12** can be synthetically advantageous as a diversity-oriented platform molecule because two chlorines and two triflates are flexibly changeable atoms for substitution reactions *via* palladium-catalyzed cross-coupling reactions.[27]

In summary, synthesis of molecular platforms enabling regio-defined preparation of fine-tuned and solution-processable DBC derivatives are achieved. The results suggest providing three salient features: One, DBC undertakes selective substitution reactions to have bis-butyl groups and two bromine units in 2,7,10,15-positions, which has materialized well-soluble, multi-tunable, and gram-scalable **1**. Two, the dibromide **1** is reactive in conventional lithiation and metal-mediated procedures, and two bromine sites are amenable to selective lithiation in one side bromine. The resultant TMS-protected **10a** works as a straightforward platform for making dissymmetric DBC derivatives. Three, the bis-phenol type **8** is amenable to regio-specific bis-chlorination, which enables us to prepare the scaffold **12** with crystallographical data. These three features will constitute a diversity-oriented approach for the fine-tuning of DBC and an illustration of the high potential of DBC skeleton in materials chemistry. Application to polymer assembly materials utilizing these scaffolds is ongoing and will be reported in due course.



Scheme 6. Synthesis of **11** and **12**.

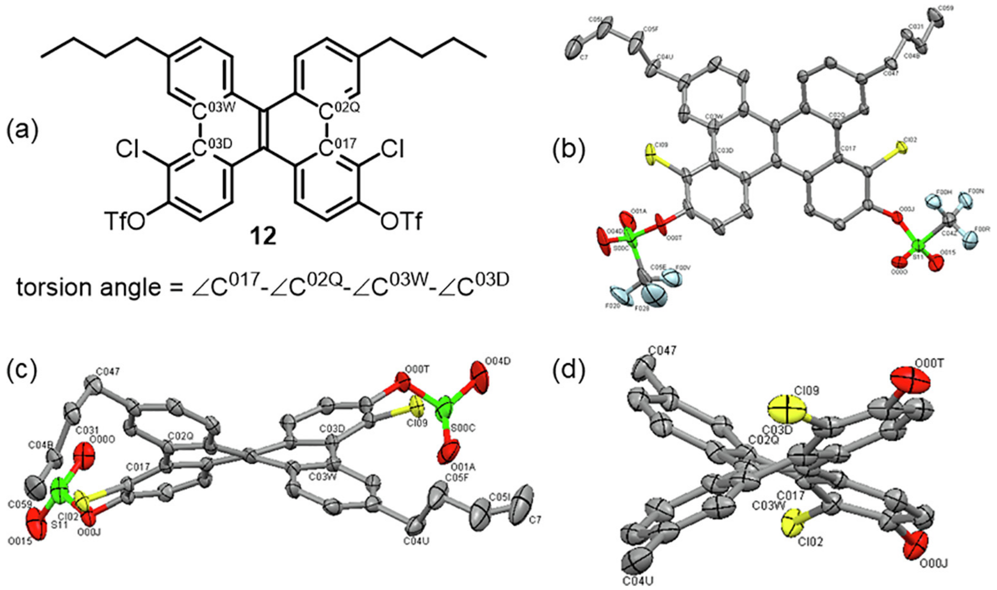


Fig. 2. Molecular structures with ORTEP drawing of **12** with thermal ellipsoids at the 50% probability level (the hydrogen atoms are omitted for clarity); (a) torsion angles determined by the four carbon atoms of C^{017}, C^{02Q}, C^{03W}, and C^{03D}; (b) top view with red of oxygens, yellow of chlorines, green of sulfurs, and pale blue of florins ; (c) side view from a butyl-groups-side fjord region with a description of the torsion angle 47° (CF$_3$ groups are omitted for ease of viewing); (c) side view from a bay-area region (Tf-substituents and C$_3$H$_7$-moieties in butyl groups are omitted for ease of viewing).

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.

Acknowledgements

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Appendix A. Supplementary data

The ^{1}H and ^{13}C NMR spectra of all new compounds. Supplementary data related to this article can be found online at https://doi.org/10.1016/j.tetlet.2020.152406.

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[14] Commercially available dibenzo[g,p]chrysene (CAS# 191-68-4) in Tokyo Chemical Industry Co., Ltd. is 1 g at the maximum amount, which costs us ¥ 44,000 (without tax).

[15] Usage of 1.5 equiv butyryl chloride gave 80% yield of 2-monoketone along with ~5% yield of 2, which suggests the second acylation in construction of 2 occurred via 2-monoketone.

[16] The regio-selectivity of the double acylation in 2 might arise from the latent polarity of 2-monoketone: its imaginary charges place minus in 7-position, and plus in 10-position; hence, the second Friedel-Crafts acylation could occur clearly in 7-position.

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[18] This crystallographical matter was solved in Figure 6.

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[25] This cyanation at 120 °C didn't complete the reaction, and the unreacted 10c remained.

[26] The single crystal of 12 was prepared by slow evaporation of acetone (0.5 mL) solution of the sample (5 mg); CCDC-2013501 (for 12) 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. Triclinic, space group P-1, colorless, a = 15.9084(2) Å, b = 21.6961(4) Å, c = 22.7683(4) Å, α = 83.769°, β = 71.662°, γ = 68.587°, V = 6942.8(2) Å3, Z = 8, T = 93 K, dcalcd. = 1.541 g cm−3, μ(Mo-Kα) = 3.513 mm−1, R1= 0.0988, wR2= 0.2572, GOF = 1.029.

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