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Rapid access to functionalized nanographenes through a palladium-catalyzed multi-annulation sequence†

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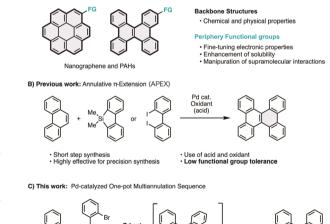
Nanographenes and polycyclic aromatic hydrocarbons exhibit many intriguing physical properties and have potential applications across a range of scientific fields, including electronics, catalysis, and biomedicine. To accelerate the development of such applications, efficient and reliable methods for accessing functionalized analogs are required. Herein, we report the efficient synthesis of functionalized small nanographenes from readily available iodobiaryl and diarylacetylene derivatives *via* a one-pot, multi-annulation sequence catalyzed by a single palladium catalyst. This method enables the preparation of small nanographenes bearing various polar functional groups, such as hydroxy, amino, and pyridinic nitrogen atoms, which are otherwise difficult to incorporate. These functional groups provide valuable sites for further derivatization, allowing the modulation of small nanographenes' solubility, optoelectronic properties, and photochromic and vapochromic behaviors. Our new method thus provides a platform for facile access to novel carbon-based materials.

Introduction

Nanographenes and polycyclic aromatic hydrocarbons (PAHs) are attractive compounds due to their unique optoelectronic properties, supramolecular behaviors, and potential applications across various fields. Since their intrinsic properties are strictly defined by their shapes, sizes, and edge structures, the chemical synthesis of nanographenes and PAHs with atomic precision has attracted significant attention from the synthetic community over the past two decades. These extensive investigations have led to the emergence of new synthetic techniques, such as annulative π -extension (APEX) reactions and on-surface syntheses, thereby enabling rapid access to structurally diverse nanographenes and PAHs.

In addition to significant progress in synthesizing fused aromatic hydrocarbons, their functionalized analogs are also attracting increasing interest (Fig. 1A).⁶ Incorporating functional groups into nanographenes expands their range of applications in materials science and chemical biology by enabling the fine-tuning of photoelectronic properties, enhancing solubility, and allowing for the manipulation of

supramolecular interactions. For instance, Aida and Fukushima reported that hexa-*peri*-hexabenzocoronene derivatives bearing long aliphatic and tetramethylene glycol chains form supramolecular nanotube architectures, resulting in distinct



Annulation Br FG Intramolecular C-H arylation Up to 75%

One-pot multi-annulation sequence without oxidant and acid
 High functinla group tolerance (including –OH, –NH₂, –COOH and pyridinic nitrogen atoms)

Fig. 1 Functionalized nanographenes and PAHs: (A) applications of functionalized nanographenes and PAHs. (B) Annulative π -extension reactions. (C) This work: Pd-catalyzed one-pot multi-annulation sequence. FG = functional group.

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photoconductivity and semiconducting properties.7 Takimiya reported that a tetramethyl-thiolated pyrene exhibits ultrahigh charge mobility as a hole-transporting material in the crystal state.8 Our group also found that a warped nanographene with tetraethylene glycol chains exhibited increased water solubility and induced cell death upon light irradiation.9 Recently, Wilson reported that pyrene tethered to an osmium complex can be programmable surface modification polymersomes.10

Although the significance of functional groups is clear, the synthesis of functionalized nanographene is not straightforward. General synthetic protocols used to access nanographenes and PAHs typically involve oxidative and/or acidic conditions, which typically result in low yields or no reaction when polar functionalities are incorporated into the substrates. Thus, available substituents are generally limited to nonpolar alkyl groups. Although the late-stage functionalization of nanographenes through halogenation,11 iridium-catalyzed C-H borylation,12 and APEX reactions3,4 provide workable protocols, issues such as substrate-dependent regioselectivity and overreaction limit the scope of these approaches to specific examples (Fig. 1B). Consequently, efficient and reliable methods for synthesizing functionalized nanographenes are in high demand.

Herein, we report a one-pot multi-annulation sequence for the synthesis of functionalized dibenzo[g,p]chrysene (DBC), a small nanographene motif, from 2-iodobiphenyls and diarylacetylenes using a single palladium catalyst (Fig. 1C). This simple yet powerful reaction enables the rapid synthesis of DBC derivatives bearing various polar functionalities, such as hydroxy groups, amino groups, and pyridinic nitrogen atoms. Additionally, we demonstrate how these functional groups can be utilized to modulate the solubility and photophysical propof the functionalized DBCs through derivatization.

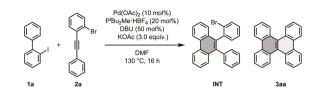
Results and discussion

Optimization of reaction conditions

Initially, we speculated that avoiding acidic or oxidative conditions would improve substrate tolerance when forming fused aromatic ring systems with polar functionalities. To establish a new efficient π -extension method with high functional group tolerance, we considered Larock's report, describing the annulation of 2-iodobiphenyl with internal alkynes to furnish 9,10diarylphenanthrene using Pd(OAc)2 and NaOAc under nearly neutral conditions.13 Given that many palladium complexes are catalysts for constructing biaryl products,14,15 we envisioned expanding palladium catalysis to a new π -extension reaction *via* a one-pot multi-annulation sequence of 2-iodobiaryls with appropriately designed diarylacetylenes, followed by intramolecular C-H arylation, to finally construct DBC frameworks.

We first identified the optimal conditions for forming DBC (3aa) using 2-iodobiphenyl (1a) and 1-bromo-2-(phenylethynyl) benzene (2a) as model substrates (Table 1). After extensive screening of reaction parameters, we discovered that 3aa was efficiently formed in a 74% NMR yield and a 67% isolated yield

Table 1 Screening of reaction conditions for the one-pot multiannulation sequence to synthesize DBC (3aa)^a



Entry	Deviation from the optimum conditions	Yield ^b (%)	
		INT	3aa
1	None	n.d.	74 (67) ^c
2	Without P ^t Bu₂Me·HBF₄	64	23
3	$PCy_3 \cdot HBF_4$ instead of $P^tBu_2Me \cdot HBF_4$	n.d.	66
4	$P^tBu_3 \cdot HBF_4$ instead of $P^tBu_2Me \cdot HBF_4$	29	37
5	PPh₃ instead of P ^t Bu₂Me⋅HBF₄	43	25
6	2,2'-bipyridyl instead of P ^t Bu ₂ Me·HBF ₄	49	29
7	Without KOAc	27	n.d.
8	K ₂ CO ₃ instead of KOAc	18	n.d.
9	KOPiv instead of KOAc	8	58
10	NaOAc instead of KOAc	24	53
11	Without DBU	n.d.	60
12	Et ₃ N instead of DBU	n.d.	50
13	Pyridine instead of DBU	n.d.	63

^a Conditions: **1a** (0.20 mmol), **2a** (1.5 equiv.), Pd(OAc)₂ (10 mol%), P^tBu₂Me·HBF₄ (20 mol%), DBU(50 mol%), KOAc (3.0 equiv.), DMF (2.0 mL), 130 °C, 16 h. b NMR yield. CH₂Br₂ was used as an internal standard. ^c Isolated yield.

when 1a and 2a were treated with $Pd(OAc)_2$, $P^tBu_2Me \cdot HBF_4$, 1,8diazabicyclo(5.4.0)undec-7-ene (DBU), and KOAc in N,N-dimethylformamide (DMF) at 130 °C for 16 h (entry 1). During ligand screening, we observed that while the ligand did not influence the annulation step, it played a crucial role in the intramolecular C-H arylation. Without a ligand, the reaction halted at the first step, resulting in the mono-annulated product INT (entry 2). However, when electron-rich alkyl phosphine ligands such as PCy₃·HBF₄ and P^tBu₃·HBF₄ were employed, the reaction proceeded to yield the desired product (entries 3 and 4). Conversely, reactions with triphenylphosphine and 2,2'-bipyridyl resulted in low yields (entries 5 and 6). In addition to the ligands, the choice of additives was found to be crucial. When the reaction was performed without KOAc, no product 3aa was observed, and a significant reduction in the amount of the intermediate (INT) was noted (entry 7). Similarly, using K₂CO₃ instead of KOAc resulted in no formation of 3aa and a reduced yield of INT (entry 8). Comparable yields were obtained when KOPiv or NaOAc were used instead of KOAc (entries 9 and 10), indicating that carboxylate anions are essential for C-H activation and annulation. The addition of DBU slightly enhanced the yield of 3aa, whereas its absence led to a reduction in yield (entry 11). Other organic bases, such as triethylamine (Et3N) and pyridine, did not influence the yield (entries 12 and 13). We postulate that DBU contributes to the efficient generation of active Pd species from the precatalyst or neutralizes the acetic acid generated during the C-H activation steps.

Scope of substrates

Having established the optimal reaction conditions, we assessed the scope of the reaction with respect to π -extending agents (Fig. 2). We first evaluated π -extending agents bearing para-functionalized arenes and found that various functional groups were compatible with this one-pot multi-annulation process. The reaction with the methoxy-substituted π -extending agent 2b yielded the corresponding product 3ab in 70% yield. The acetoxy group, which is susceptible to hydrolysis under basic conditions, afforded the deacetylated product 3ac directly in 69% yield. The π -extending agent bearing a nonprotected amine (2d), a challenging functional group in Pd catalysis, furnished DBC-NH2 (3ad) in 30% yield. Electronwithdrawing substituents such as Cl, CN, and CF3 groups were also tolerated, delivering the corresponding products in yields of 62–75% (3ae-ag). We then explored π -extending agents with meta-substituted arenes (2h-k). For substrates with electron-donating groups, the corresponding products 3ah-ak

were afforded as mixtures of separable regioisomers, often in equal or higher yields compared to those with para-substituted π -extending agents. In contrast to the general regionelectivity observed in C-H activation via the concerted metalationdeprotonation (CMD) pathway,15 which typically favors the most acidic or sterically accessible C-H bond, the sterically hindered product was obtained as the major isomer. This trend in reactivity and regioselectivity can be attributed to the proximal guidance by the coordinating functional groups during the C-H activation process.16 In contrast, electron-withdrawing groups, such as acetyl and carboxylic acids, exhibited the opposite regioselectivity, likely due to increased steric hindrance. The compatibility of coordinative heteroaromatic rings is notable; reactions with π -extending agents bearing 4pyridyl (21), 3-pyridyl (2m), 5-pyrimidyl (2n), and 3-quinolinyl (20) produced the corresponding aza-DBCs 3al-ao in good yields, in the range of 47-75%. Further investigations focused on utilizing the present method to construct larger structures

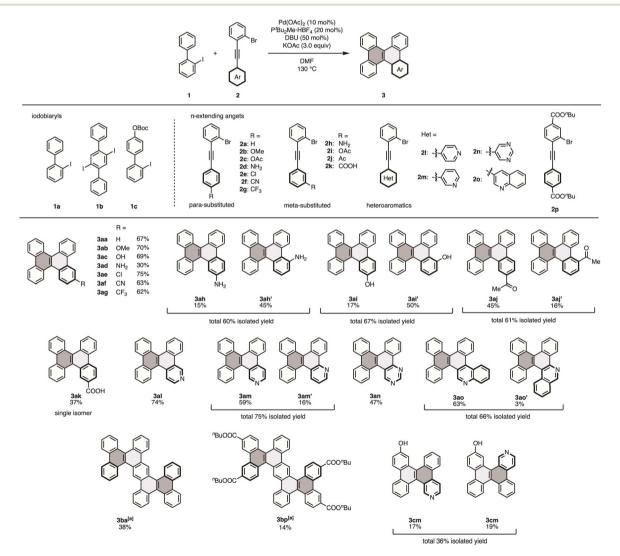


Fig. 2 Scope of substrates for the Pd-catalyzed one-pot multi-annulation sequence. Conditions: (1) (0.20 mmol, 1.0 equiv.), (2) (1.5 equiv.), Pd(OAc)₂ (10 mol%), P^tBu₂Me·HBF₄ (20 mol%), DBU (50 mol%), KOAc (3.0 equiv.), DMF (2.0 mL), 130 °C, 16 h. ^a3.0 equiv. π -extending agent, 20 mol% Pd(OAc)₂, 40 mol% P^tBu₂Me·HBF₄, 1.0 equiv. DBU were used.

and bifunctionalized derivatives. When 2',5'-diiodo-1,1':4',1''-terphenyl (1b) was employed instead of 1a, the reaction with 2a afforded the doubly extended product 3ba in 38% yield. Moreover, its functionalized analog 3bp was synthesized via the double π -extension of 1b with 2p, although in a low yield. Bocprotected substrate 1c reacted with 2m to yield bifunctional DBC analogs 3cm and 3mc' as deprotected forms, in 17% and 19% yields, respectively. Overall, this novel π -extension method exhibits broad functional versatility and holds potential for the synthesis of a range of functionalized nanographene structures.

Further derivatization of 3ah' and 3cm

The properties of functionalized DBCs can be further modified through additional derivatization (Fig. 3). For instance, aminated DBC 3ah' was reacted with carboxylic acid via a general condensation procedure to yield 3ah'-amide in 82% yield. Unlike unfunctionalized DBC, 3ah'-amide remained in a liquid state at room temperature and displayed improved solubility in polar solvents. Furthermore, 3ah' was coupled with 4-iodoaniline after nitrosation with m-chloroperbenzoic acid (mCPBA), producing 3ah'-azobenzene, which has potential applications in photoswitching materials. The Sandmeyer reaction was also used to convert 3ah' into iodinated DBC 1d with a yield of 62%. This iodinated DBC was then used in a multi-annulation sequence with 21, resulting in 3dl in 10% yield; 3dl is a heterocyclic analog of hexabenzo[a,c,fg,j,l,op]tetracene (HBT), known for its excellent hole-transporting properties in OLEDs.17 In addition, 3am was functionalized with various alkyl electrophiles to form ionic DBCs. Reaction with mPEG4Br produced 3am-PEG4[†]Br⁻ as a gel-like yellow semisolid in quantitative

yield. Treatment with 1,6-dibromohexane resulted in the formation of the ionic dimer 3a in 74% yield. A similar protocol was applied for bifunctional DBC 3cm, yielding the zwitterionic species 3cm-Me. Among these ionic DBC derivatives, 3am-PEG4⁺Br⁻ displayed excellent solubility in various organic solvents and aqueous media. This dramatic enhancement in solubility can be attributed to the ionic nature of the pyridinium moiety and the hydrophilic triethylene glycol chain.

Photophysical properties of functionalized DBCs

Selected UV-vis absorption spectra of the functionalized DBCs in dry DMF solution (6.87–7.50 \times 10⁻⁵ M) are shown in Fig. 4. Compounds 3am and 3cm displayed intense absorption bands with the longest absorption maxima at 352 and 355 nm, respectively (Fig. 4 and ESI). These absorption profiles closely resemble those of the parent DBC in dichloromethane solution,18 indicating that nitrogen-doping and hydroxylation have minimal impact on the DBC structure's absorption characteristics. In contrast, 3am-PEG4+Br exhibited a red-shifted absorption band, with the longest wavelength absorption maximum at 421 nm. DFT calculations at the B3LYP/6-31+G(d) level estimated the HOMO and LUMO energy levels of 3am to be -5.761 eV and -1.94 eV, respectively, while for 3am-PEG4⁺Br⁻, the values were -8.722 eV and -5.791 eV (see ESI†). The redshifted absorption is likely due to a significant decrease in the LUMO energy level relative to the HOMO upon N-alkylation, leading to a narrow HOMO-LUMO energy gap. In addition, 3cm-Me showed a further red-shifted absorption band with a weak broad absorption between 480 and 700 nm, attributed to intramolecular charge transfer.19 This weak absorption band

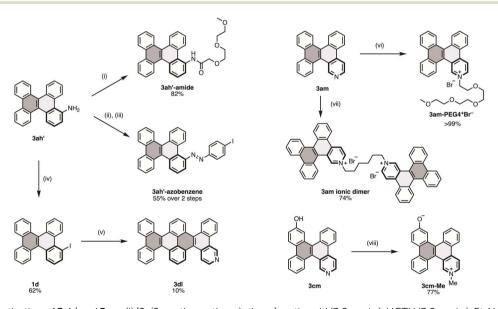


Fig. 3 Further derivatization of 3ah' and 3am. (i) [2-(2-methoxyethoxy)ethoxy]acetic acid (3.0 equiv.), HCTU (3.0 equiv.), Et₃N (5.7 equiv.), DMF, rt, 26 h, 82% yield; (ii) mCPBA (3.1 equiv.), toluene, rt, 0.5 h, 81% yield; (iii) 4-iodoaniline (3.0 equiv.), $CH_2Cl_2/AcOH$, 60 °C, 24 h, 68% yield; (iv) NaNO₂ (1.7 equiv.), conc. HCl, 0 °C, 2 h, then KI (10 equiv.), rt, 12 h, 62% yield; (v) 2l (1.7 equiv.), Pd₂(dba)₃·CHCl₃ (5 mol%), KOAc (3.0 equiv.), DMF, 130 °C, 12 h, then additional Pd₂(dab)₃·CHCl₃ (5 mol%), PfBu₂Me·HBF₄ (40 mol%), DBU (1.0 equiv.), 150 °C, 3.5 h, 10% yield; (vi) mPEG4Br (3.9 equiv.), DMF, 90 °C, 20 h, >99% yield; (vii) 1,6-dibromohexane (0.5 equiv.), DMF, 90 °C, 12 h, 74% yield (viii) MeI (1.1 equiv.), DMF, 90 °C, 2.5 h, then NBu₄OH (1.0 equiv.), MeOH/DMSO, 5 min, 77% yield. HCTU = 2-(6-chloro-1*H*-benzotriazole-1-yl)-1,1,3,3-tetramethylammonium hexafluorophosphate; dba = dibenzylideneacetone; mPEG4Br = triethylene glycol 2-bromoethyl methyl ether.

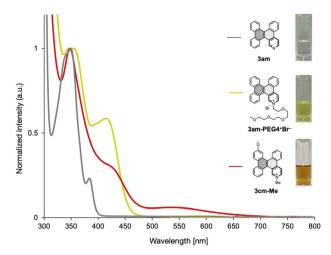


Fig. 4 UV-vis absorption spectra of **3am**, **3am-PEG4⁺Br**⁻, and **3cm-Me** in dry DMF solution.

was attenuated when a mixture of dry DMF and H_2O (99:1, v/v) was used as the solvent, and was completely diminished in a DMF/AcOH (99:1, v/v) solution (Fig. 5A). Sensitivity to water and acid was even more pronounced in the solid state (Fig. 5B). The solid form of **3cm-Me** changed color from dark brown to orange when exposed to atmospheric moisture and reverted to dark brown after 30 min under vacuum. Upon exposure to AcOH vapor, the orange solid of **3cm-Me** irreversibly turned yellow, corresponding to the protonated state. This vapochromic behavior in response to humidity and acid vapor demonstrates the potential of **3cm-Me** as a vapor-sensing material.²⁰

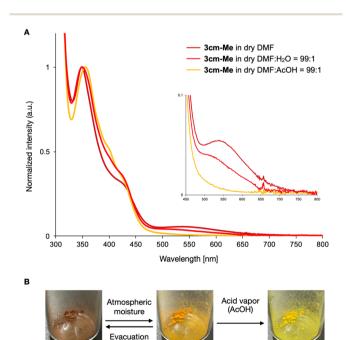


Fig. 5 Water and acid response behavior of **3cm-Me**. (A) Water and acid responsive absorption changes in solution. (B) Moisture and acid vapor responsive color changes in the solid state.

Conclusions

In summary, we established an efficient approach for functionalizing nanographenes and PAHs via a Pd-catalyzed onepot, multi-annulation sequence. The combination Pd(OAc)₂/P^tBu₂Me·HBF₄/KOAc effectively promotes both the annulation of 2-iodobiphenyls with diarylacetylenes and subsequent intramolecular C-H arylation, leading to the formation of the DBC framework. The high functional group tolerance of this one-pot sequence allows rapid access to a range of functionalized DBCs bearing amino, hydroxy, and carboxylic acid groups, as well as pyridinic nitrogens-compounds that are challenging to synthesize using previous π -extension methods. We also demonstrated that these functional groups serve as reliable reactive sites for further derivatization, yielding azobenzene, azananographene, and ionic DBCs. UV-vis absorption spectra and DFT calculations of the ionic DBCs indicate that N-alkylation significantly affects their photophysical properties. Additionally, we revealed the unique vapochromic properties of the zwitterionic DBC. Overall, the method developed in this study serves as a reliable platform for facile access to novel carbon-based materials.

Data availability

The data supporting the findings of this study are available in the ESI material. \dagger

Author contributions

T. M. and K. I. conceived and designed the research. T. M. performed experiments and collected the data. T. M. and K. I. wrote the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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