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Palladium-catalyzed direct phenylation of perylene: structural and optical properties of 3,4,9-triphenylperylene and 3,4,9,10-tetraphenylperylene

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ABSTRACT

We have developed one-step synthesis of multiphenylperylenes from perylene through palladium-catalyzed oxidative C–H/C–B coupling using phenylboroxin as a phenyl source. The combination of $Pd(OAc)_2$ as a catalyst and *o*-chloranil as an oxidant is the key for direct C–H arylation of perylene. The X-ray crystallography of 3,4,9-triphenylperylene (**3**) and 3,4,9,10-tetraphenylperylene (**4**) revealed twisted structures of perylene core caused by steric repulsion of neighboring phenyl groups. Compounds **3** and **4** showed red shift in both absorption and fluorescence spectra compared to perylene whereas absolute fluorescence quantum yields are similarly high (Φ_F=0.94).

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are of significant importance in the field of materials science and nanocarbon chemistry not only because of their electronic and photophysical properties but also because they can be considered as small segments of graphenes. Arylation of PAHs is a fundamental reaction to tune the properties of PAHs.[1] Typical method for arylation of PAHs can be categorized into halogenation of PAHs followed by Pd-catalyzed cross-coupling reactions[2] or Ir-catalyzed C–H borylation of PAHs followed by Pd-catalyzed cross-coupling with aryl halides.[3] Although direct C–H arylation of PAHs is widely sought by materials science, there have been few reports on C–H/C–M coupling (M=Sn, Si) of PAHs[4] except our work. Recently, we have discovered that $Pd(OAc)_2$/*o*-chloranil catalyst can promote a C–H arylation of PAHs with arylboron compounds (C–H/C–B coupling) (Fig. 1).[5] The C–H arylation takes place regioselectively at the K-region of pyrene, phenanthrene, and benzo[*a*]anthracene.[5a] The $Pd(OAc)_2$/*o*-chloranil catalyst system is also applicable to C–H/C–B, C–H/C–Si and C–H/C–H coupling of fluoranthene with high regioselectivity.[5b] More recently, we found that corannulene, a bowl-shaped PAH having K-regions, can be subjected to the C–H arylation under the influence of $Pd(OAc)_2$/*o*-chloranil to furnish decaarylcorannulenes, in which corannulene cores are unusually flattened.[5c] Furthermore, we have demonstrated two-step π-extension of PAHs through the sequence of direct arylation and dehydrogenative cyclization.[5a,b]

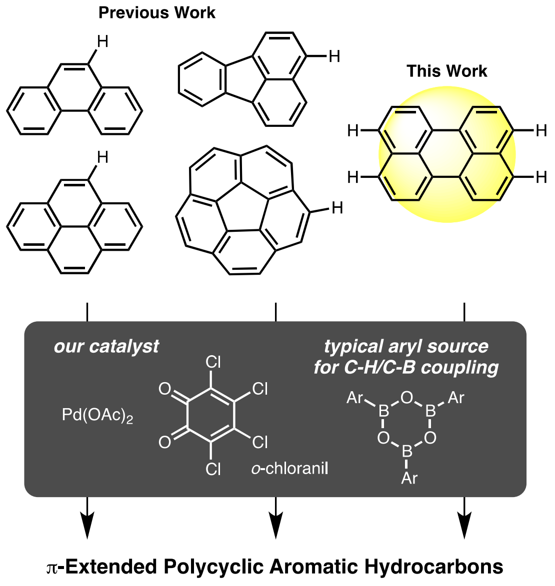

Fig. 1. Palladium-catalyzed direct C–H arylation of PAHs.

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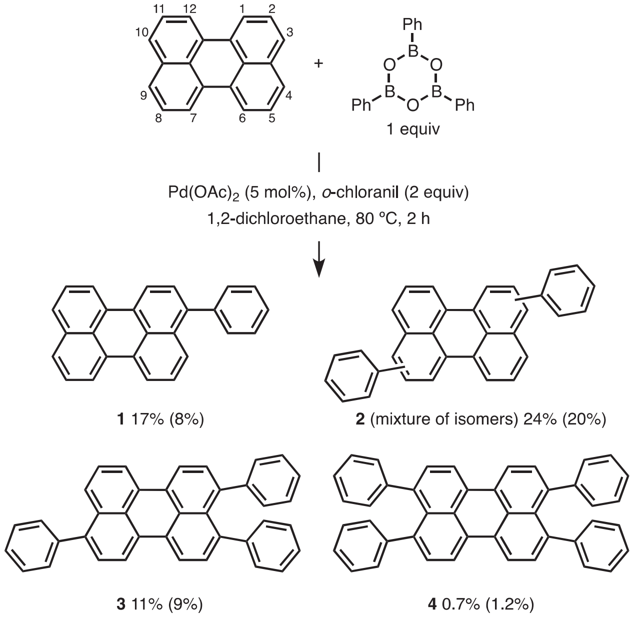
In this paper we report on the arylation of perylene with phenylboroxin catalyzed by $Pd(OAc)_2$/*o*-chloranil. Perylene derivatives, representative of which is perylene bisimides, have found various applications as optical and electrical materials.[6,7] However, functionalization of perylenes are still limited to halogenation[1] and borylation.[3a] Thus, the development of a direct and selective perylene arylation protocol is highly called for and should have a great impact in materials science. The outcome of our extensive investigations is the first one-step synthesis of multiphenylperylenes from perylene through palladium-catalyzed oxidative C–H/C–B coupling using phenylboroxin as a phenyl source. Structural and photophysical properties of tri- and tetraphenylperylenes are also discussed.

2. Results and discussion

2.1. Direct multi-phenylation of perylene

We began by applying our standard conditions of C–H/C–B coupling to pyrene.[5a] Thus, the treatment of perylene (1 equiv) and phenylboroxin (1 equiv) in the presence of $Pd(OAc)_2$ (5 mol %) and *o*-chloranil (2 equiv) in 1,2-dichloroethane at 80 °C produced 3-phenylperylene (**1**) in 17% isolated yield (Scheme 1). Concurrently, di-, tri-, and tetraphenylated perylenes (**2**, **3**, and **4**) were also obtained in 24%, 11%, and 0.7% yield, respectively. The yield of diphenylperylene **2** was determined as the mixture of isomers. The C–H/C–B coupling took place selectively at the peri-positions (C3, C4, C9, and C10) of perylene similar to the C3-selective arylation of fluoranthene, which we previously reported.[5b] The yields of **3** and **4** did not increase dramatically even larger amounts of phenylboroxin (1.67 equiv), $Pd(OAc)_2$ (20 mol %), and *o*-chloranil (4 equiv) were employed (Scheme 1, yields shown in parentheses). These results indicate that the third and fourth phenylation reactions are relatively slow due to steric hindrance of phenyl groups on the peri-positions. The structures of phenylated perylenes were identified by ^{1}H NMR, ^{13}C NMR, and HRMS.



Scheme 1. Pd-catalyzed C–H/C–B coupling of perylene and phenylboroxin. Yields are isolated yields. Values in parenthesis are the yields resulted from following conditions: $Pd(OAc)_2$ 20 mol %, phenylboroxin 1.67 equiv, *o*-chloranil 4 equiv.

2.2. X-ray crystal structures of 3,4,9-triphenylperylene and 3,4,9,10-tetraphenylperylene

The structures of **3** and **4** were unambiguously confirmed by X-ray crystallography. The X-ray crystal structures of **3** and **4** are shown in Fig. 2. Center of symmetry is located on the center of molecule **4**. It is clearly seen that perylene core of **3** is twisted with the torsion angle of around 10° owing to steric repulsions between two phenyl rings. Interestingly, perylene core of **4** is not as twisted as **3**, but rather adopts interesting bent structure as a whole. The phenyl groups at 3- and 10-positions are directed toward the same direction perpendicular to the perylene plane, whereas the phenyl groups at 4- and 9-positions are directed toward other direction. The distances between ipso-positions of neighboring phenyl rings are 2.996(7) Å for **3** and 2.961(2)/2.952(2) Å for **4**, which indicate that steric repulsions of phenyl rings of **3** and **4** are similar. In the solid state of both **3** and **4**, molecules are located far from each other (longer distances than sum of van der Waals radii). These results indicate that there is no significant intermolecular π–π interactions in **3** and **4** due to the steric hindrance of phenyl groups.

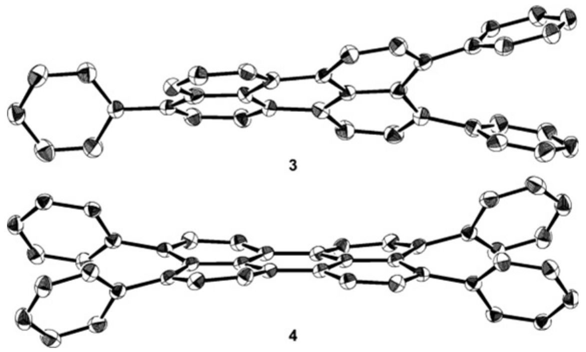


Fig. 2. ORTEP drawings of **3** (top) and **4** (bottom) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. One of two independent molecules of **4** is shown.

2.3. Photophysical properties of 3,4,9-triphenylperylene and 3,4,9,10-tetraphenylperylene

The electronic absorption and fluorescence properties of **3** and **4** in dichloromethane were investigated, including UV–vis absorption, fluorescence spectra, and fluorescence quantum yields. The absorption and fluorescence spectra of **3** (blue) and **4** (red) are shown in Fig. 3 and the data are summarized in Table 1. As a reference, the UV–vis absorption of parent perylene is also shown (gray) in Fig. 3. The absorption spectra of **3** and **4** are broadened compared with that of perylene. The absorption coefficients (ε) of **3** and **4** were determined to be 3.7×10^4 and 4.2×10^4 M^{-1} cm^{-1}, respectively. As somewhat expected, we observed bathochromic shift in absorption maximum (λ_{max}) as the number of phenyl groups increased; 436 nm (perylene) <473 nm (**3**) <486 nm (**4**). Both **3** and **4** showed intense photoluminescence in solution with the emission maximum wavelengths (λ_{em}) of 500 nm and 520 nm, respectively. The absolute fluorescence quantum yields (Φ_F) of **3** and **4** in dichloromethane were found to be extremely high (0.94 for both compounds). Although X-ray crystallographic analysis clearly showed the structural difference between **3** and **4**, significant difference of absorption and fluorescence between **3** and **4** was not observed. It is presumed that the two conformations of perylene cores, twisted or planar, are interconverted rapidly in solution state.

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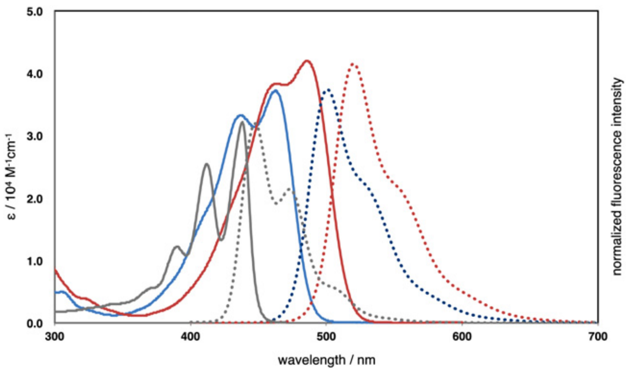

Fig. 3. UV–vis absorption (solid line) and fluorescence spectra (broken line) of perylene (gray), **3** (blue) and **4** (red) in dichloromethane. Fluorescence spectra are normalized.

Table 1
Photophysical data for perylene, **3**, and **4**[a]

Compound	Absorption		Fluorescence	
	ε [M^{-1} cm^{-1}][b]	λ_{max} [nm][b]	λ_{em} [nm][c]	Φ_F[d]
Perylene	3.2×10^4	438	448	0.97[e]
3	3.7×10^4	473	500	0.94
4	4.2×10^4	486	520	0.94

[a] In dichloromethane.
[b] Only the longest absorption maxima are given.
[c] Emission maxima upon excitation at the absorption maximum wavelengths (λ_{max}).
[d] Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within ±3% errors.
[e] A value reported in Ref. 8.

3. Conclusion

We have developed one-step synthesis of multiphenylperylenes from perylene through palladium-catalyzed oxidative C–H/C–B coupling using phenylboroxin as a phenyl source. The combination of Pd(OAc)$_2$ as a catalyst and *o*-chloranil as an oxidant is the key for direct C–H arylation of perylene. Although the yield of each phenylated perylene is not high, our newly developed method represents the most step-economical way to supply arylated perylenes. The X-ray crystallography of 3,4,9-triphenylperylene (**3**) and 3,4,9,10-tetraphenylperylene (**4**) revealed twisted structures of perylene core caused by steric repulsion of neighboring phenyl groups. Compounds **3** and **4** showed red shift in both absorption and fluorescence spectra compared to perylene whereas absolute fluorescence quantum yields are similarly high (Φ_F=0.94). Further investigation on the sequential π-extension of perylene for the concise transformation of rylenes[9] is now ongoing.

4. Experimental section

4.1. General

All materials including dry solvents were obtained from commercial suppliers and used without further purification. Phenylboroxin was prepared from phenylboronic acid by reported procedure.[10] All reactions were performed with dry solvents under an atmosphere of argon in dried glassware with standard vacuum-line techniques. Work-up and purification procedures were carried out with reagent-grade solvents under air.

High-resolution mass spectra (HRMS) were measured on a JMS-T100TD instrument (DART). Melting points were measured on a MPA100 Optimelt automated melting point system. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECS-600 (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.0 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, m=multiplet), coupling constant (hertz), and integration.

4.2. Procedure for direct C–H phenylation of perylene

A solution of Pd(OAc)$_2$ (11.2 mg, 50 μmol, 5.0 mol %), *o*-chloranil (490 mg, 2.0 mmol, 2.0 equiv), perylene (252 mg, 1.0 mmol, 1.0 equiv), and phenylboroxin (311 mg 1.0 mmol, 1.0 equiv) in dry 1,2-dichloroethane (20 mL) was stirred at 80 °C for 2 h. After cooling the reaction mixture to room temperature, the mixture was passed through a short pad of silica gel (CH_2Cl_2, 100 mL). The filtrate was then evaporated and the residue was purified by silica gel column chromatography (hexane/CH_2Cl_2=100:0 to 85:15) to obtain 3-phenylperylene (**1**) (56.2 mg 17%), mixture of diphenylperylene isomers (**2**) (97.5 mg, 24%), 3,4,9-triphenylperylene (**3**) (54.2 mg, 11%), and 3,4,9,10-tetraphenylperylene (**4**) (3.7 mg, 0.7%).

4.3. Compound data of products

*4.3.1. 3-Phenylperylene (**1**).* ^{1}H NMR (600 MHz, $CDCl_3/CS_2$=1:1) δ 8.20 (d, *J*=8.4 Hz, 1H), 8.18 (d, *J*=6.6 Hz, 2H), 8.17 (d, *J*=6.6 Hz, 1H), 7.73 (d, *J*=7.8 Hz, 1H), 7.66 (d, *J*=7.8 Hz, 2H), 7.49–7.45 (m, 6H), 7.42–7.39 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$=1:1) δ 140.6, 139.9, 134.6, 132.9, 131.33, 131.28, 131.2, 130.5, 129.9, 129.0, 128.6, 128.3, 127.74, 127.70, 127.65, 127.3, 126.6, 126.45, 126.0, 120.31, 120.28, 120.1, 119.9. HRMS (DART, ESI$^+$) *m*/*z* calcd for $C_{26}H_{17}$ $[M+H]^+$: 329.1330, found: 329.1329. Mp: 197.4–199.4 °C.

*4.3.2. 3,4,9-Triphenylperylene (**3**).* ^{1}H NMR (600 MHz, $CDCl_3/CS_2$=1:1) δ 8.24 (d, *J*=7.8 Hz, 1H), 8.23 (d, *J*=7.8 Hz, 1H), 8.21 (d, *J*=7.8 Hz, 1H), 8.19 (d, *J*=7.8 Hz, 1H), 7.74 (d, *J*=7.8 Hz, 1H), 7.49–7.45 (m, 4H), 7.42–7.37 (m, 5H), 6.96 (d, *J*=7.2 Hz, 4H), 6.89 (t, *J*=7.2 Hz, 4H), 6.84 (d, *J*=7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$=1:1) δ 142.9, 140.4, 140.01, 139.98, 139.6, 132.5, 131.5, 131.4, 130.61, 130.59, 130.56, 130.5, 130.4, 129.8, 129.4, 128.4, 128.2, 127.8, 127.2, 126.6, 125.8, 125.7, 120.4, 120.3, 120.1, 120.0. HRMS (DART, ESI$^+$) *m*/*z* calcd for $C_{38}H_{25}$ $[M+H]^+$: 481.1956, found: 481.1955. Mp: 251.1–253.1.

*4.3.3. 3,4,9,10-Tetraphenylperylene (**4**).* ^{1}H NMR (600 MHz, $CDCl_3/CS_2$=1:1) δ 8.30 (d, *J*=7.8 Hz 4H), 7.43 (d, *J*=7.8 Hz 4H), 7.00 (d, *J*=6.6 Hz, 8H), 6.91 (t, *J*=7.2 Hz, 8H), 6.87 (t, *J*=7.4 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3/CS_2$=1:1) δ 142.8, 140.0, 131.7, 130.7, 130.4, 130.1, 129.4, 127.2, 125.7, 120.4. HRMS (DART, ESI$^+$) *m*/*z* calcd for $C_{44}H_{29}$ $[M+H]^+$: 557.2269, found: 557.2243. Mp: >300 °C.

4.4. X-ray crystal structure analysis of 3 and 4

Intensity data were collected at 103(2) K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with graphite-monochromated Mo *Kα* radiation (λ=0.71070 Å). The structure was solved by direct methods (SIR-97)[11] and refined by the full-matrix least-squares techniques against F^2 (SHELXL-97).[12] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

Details of the crystal data and a summary of the intensity data collection parameters for **3** (CCDC 881424): a total 14,954 reflections were corrected, of which 3893 were independent reflections (R_{int}=0.0881). $C_{38}H_{24}$, *FW*=480.57, crystal size $0.10\times0.03\times0.01$ mm^3, orthorhombic, space group $Pca2_1$,

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a=9.162(2) Å, b=18.927(5) Å, c=13.446(3) Å, V=2331.8(10) Å^3, Z=4, D_{calcd}=1.369 g/cm^3. The refinement converged to R_1=0.0689, wR_2=0.1584 ($I>2\sigma(I)$), R_1=0.1102, wR_2=0.1939 (for all data), GOF=1.063.

Details of the crystal data and a summary of the intensity data collection parameters for **4** (CCDC 881425): a total 17,839 reflections were corrected, of which 4943 were independent reflections (R_{int}=0.0403). $C_{44}H_{28}$, FW=556.66, crystal size 0.15×0.05×0.05 mm^3, monoclinic, space group $P2_1/n$. a=14.822(3) Å, b=10.855(2) Å, c=17.836(4) Å, β=99.744(3)°, V=2828.3(9) Å^3, Z=4, D_{calcd}=1.307 g/cm^3. The refinement converged to R_1=0.0490, wR_2=0.1153 ($I>2\sigma(I)$), R_1=0.0643, wR_2=0.1265 (for all data), GOF=1.079.

4.5. Photophysical property measurements

UV–vis absorption spectra were recorded on a Shimadzu UV-3510 spectrometer with a resolution of 0.5 nm. Emission spectra were measured with an F-4500 Hitachi spectrometer with a resolution of 0.2 nm. Dilute solutions in degassed spectral grade chloroform in a 1 cm square quartz cell were used for measurements. Absolute fluorescence quantum yields were determined with a Hamamatsu C9920-02 calibrated integrating sphere system. Fluorescence lifetimes were measured with a Hamamatsu Picosecond.

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Supplementary data

Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds **1**, **3**, **4** are available. Supplementary data related to this article can be found online athttp://dx.doi.org/10.1016/j.tet.2013.01.037.

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