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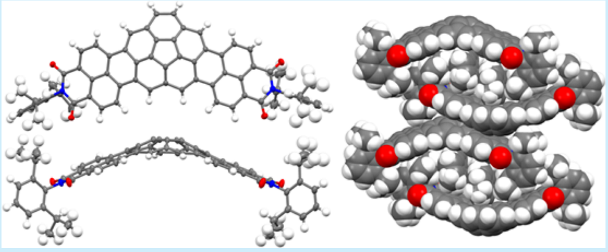
Electron-Poor Bowl-Shaped Polycyclic Aromatic Dicarboximides: Synthesis, Crystal Structures, and Optical and Redox Properties

Kazutaka Shoyama,[†] David Schmidt,[†,‡] Magnus Mahl,[†] and Frank Würthner*[,†,‡]

[†]Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany
[‡]Center for Nanosystems Chemistry (CNC), Universität Würzburg, Theodor-Boveri-Weg, 97074 Würzburg, Germany

S *Supporting Information*

ABSTRACT: Two new bowl-shaped polycyclic aromatic hydrocarbons, based on corannulene and naphthalene dicarboximide, are synthesized by an improved Suzuki−Miyaura cross-coupling and C−H arylation cascade reaction. Crystallographic analyses confirm structural assignments and provide insight into molecular interactions in the solid state. The new bowl-shaped molecules show reversible oxidation and reduction, intense visible range absorption, and high fluorescence quantum yields. These molecules can be considered bowl-shaped congeners of planar perylene dicarboximides.



The discovery of fullerenes and carbon nanotubes has motivated the pursuit of nonplanar polycyclic aromatic hydrocarbons (PAHs).[1−5] In particular, bowl-shaped PAHs are attractive synthetic targets. Interest in curved aromatic scaffolds continues to increase because such systems offer high prospects for packing control as desired in organic materials and supramolecular chemistry (e.g., in bulk heterojunction solar cells,[6,7] liquid crystals,[8,9] supramolecular polymerization,[10] and host−guest complexation).[11−13] Being commercially available and mass-producible,[14] corannulene has become the most utilized precursor for bowl-shaped PAHs and has been functionalized with various moieties.[15,16] Simple groups are introduced by nucleophilic substitution,[17,18] metal-catalyzed C−C bond formation,[18−21] or Rieche formylation.[22] As well, substituents may be installed prior to constructing the corannulene scaffold.[21,23,24] Extension of the corannulene π-scaffold is achieved by introduction of electron-rich aromatic substituents followed by direct arylation[25] or oxidative condensation.[26−28] However, it is challenging to expand the corannulene π-scaffold with electron-deficient substituents by the above-mentioned synthetic methods.[29] We reasoned that our recently introduced Pd-catalyzed Suzuki−Miyaura cross-coupling/C−H arylation cascade protocol for 4,5-dibromo-1,8-naphthalene dicarboximides and aromatic boronic esters could be applied to corannulene π-scaffold extension.[30,31] This would afford hitherto unknown, but highly desirable, bowl-shaped electron-deficient PAHs with potential applications in electric-field responsive dipolar materials[9,32] or as n-type semiconductors.[27]

Here we report the first examples for this unknown class of bowl-shaped electron-poor PAHs that comprise corannulene and one or two naphthalene dicarboximide moieties (**1** and **2**, Figure 1). These compounds were obtained by a modification of our previously reported cascade annulation reaction using reaction conditions that favorably effect Heck-type reactions.[33] The molecular structures of the newly synthesized bowl-shaped PAHs were unequivocally assigned by X-ray crystallographic analysis. Interestingly, while monoannulated shovel-like bowl **1** exhibits one-dimensional columnar bowl-in-bowl packing commonly seen for bowl-shaped PAHs,[12,13,20,24] diannulated bowl **2** forms a solvent-incorporated sandwich motif.

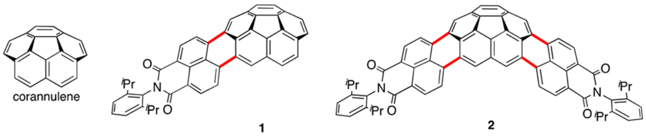


Figure 1. Structures of corannulene and the first examples of bowl-shaped polycyclic aromatic dicarboximides **1** and **2**.

We first targeted the synthesis of monoannulated bowl **1** by optimizing the reaction conditions for Pd-catalyzed cascade Suzuki−Miyaura cross-coupling and direct arylation between literature-known dibromo-naphthalene dicarboximide **4**[34] and corannulene monoboronic ester **3** (Scheme 1). Boronic ester **3** was prepared according to a literature-reported iridium-catalyzed C−H borylation procedure.[15,16] To our disappointment, only traces of the desired product **1** could be observed when our previously successful annulation method[30,31] was applied (Table 1, entry 1). Fortunately, after optimization of the phosphine ligand, reaction of boronic ester **3** and dibromonaphthalene dicarboximide **4** using $[Pd_2(dba)_3]\cdot CHCl_3$ as a Pd(0) source, $P(o\text{-tolyl})_3$ as a ligand, and Cs_2CO_3 as a base at 90 °C gave bowl **1** in 36% isolated yield (Table 1, entries 2−4).

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Scheme 1. Synthesis of Bowl-Shaped Polycyclic Aromatic Dicarboximide 1

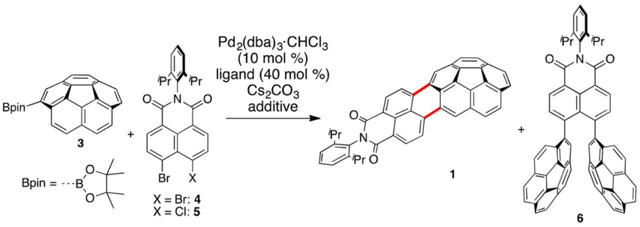


Table 1. Optimization of Reaction Conditions for Scheme 1[a]

entry	condition	ligand	additive	yield[b] (%) 1	yield[b] (%) 6
1	A	SPhos	–	traces	traces
2	A	HBF$_4$·PCy$_3$	–	19	20
3	A	P(mesityl)$_3$	–	11	18
4	A	P(*o*-tolyl)$_3$	–	36[c]	12
5[d]	A	P(*o*-tolyl)$_3$	–	24	12
6[e]	A	P(*o*-tolyl)$_3$	–	14	19
7[f]	A	P(*o*-tolyl)$_3$	–	6	29[c]
8	A	P(*o*-tolyl)$_3$	Bu$_4$NCl	15	28
9	A	P(*o*-tolyl)$_3$	Bu$_4$NBr	11	26
10	B	P(*o*-tolyl)$_3$	–	29	n.d.
11	B	P(*o*-tolyl)$_3$	Bu$_4$NCl	41[c]	n.d.
12	B	P(*o*-tolyl)$_3$	LiCl	17	n.d.
13	B	P(*o*-tolyl)$_3$	CsOPiv	18	n.d.

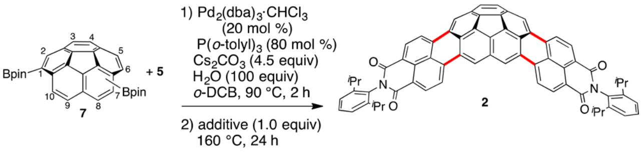
[a] Condition A: **3** (0.04 mmol), **4** (1.5 equiv), [Pd$_2$(dba)$_3$]·CHCl$_3$ (10 mol %), ligand (40 mol %), Cs$_2$CO$_3$ (1.5 equiv), toluene/water (2:1), 90 °C, 12 h. Condition B: **3** (0.04 mmol), **5** (1.0 equiv), [Pd$_2$(dba)$_3$]·CHCl$_3$ (10 mol %), ligand (40 mol %), Cs$_2$CO$_3$ (3.0 equiv), water (100 equiv), *o*-DCB, 90 °C, 2 h, then added additive (0.5 equiv), 160 °C, 24 h. [b] Yield determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. [c] Isolated yield. [d] Dry toluene was used as solvent instead of toluene/water mixture. [e] Corannulene boronic acid was used instead of ester **3**. [f] 2.5 mol % of catalyst and 10 mol % of ligand were used. *o*-DCB: *o*-dichlorobenzene. SPhos: 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl. n.d.: not detected.

The main side product of this reaction was di(corannulenyl)-naphthalene dicarboximide **6**, which indicates that intermolecular Suzuki–Miyaura reaction is competing with an intramolecular direct arylation reaction. In accordance with this, we also observed increased amounts of **6** when we used corannulene boronic acid instead of ester **3** or employed a lower catalyst concentration (Table 1, entries 6, 7). Attempts to promote the direct arylation reaction by adding quaternary ammonium salts[35] failed, possibly because these salts also promote competing Suzuki–Miyaura couplings (Table 1, entries 8, 9).

In order to suppress this side reaction we examined a stepwise cascade reaction using a newly synthesized bromo-chloro-naphthalene dicarboximide **5** (see Supporting Information (SI) for synthesis). The first-step Suzuki–Miyaura cross-coupling was performed at 90 °C, and the subsequent arylation was performed *in situ* at 160 °C (Table 1, entries 10–13). Additives that assist the Heck reaction or direct arylation reaction were also tested. We found that tetrabutylammonium chloride has a positive effect on this cascade, and bowl **1** was isolated in an improved yield of 41%. Another chloride salt, LiCl, did not exert a significant effect, possibly due to the lower solubility of lithium salts in organic solvents. Pivalate, which can also coordinate to Pd(II) and is known to positively assist various direct arylation reactions by concerted metalation–deprotonation,[36] did not improve the yield of **1**. This implies that concerted metalation–deprotonation is not the likely mechanism for this direct arylation reaction.[37]

With the optimized reaction conditions for **1** we were also able to synthesize diannulated bowl-shaped PAH **2**. Pd-catalyzed reaction of chloro-bromo-naphthalene dicarboximide **5** and diboronic acid diester **7** gave bowl **2** in 31% isolated yield (Scheme 2). Effects of additives were similar to those for the onefold annulation. Diboronic diester **7** was prepared similarly to **3** by adjusting the stoichiometry of bis(pinacol)ester and was isolated as a regioisomeric mixture after column chromatography. The composition of **7** was confirmed by mass spectrometry (MALDI-TOF) and elemental analysis (see SI). We note here that the above-mentioned iridium catalysis is sensitive to steric effects[38] and therefore the two boronic ester moieties in **7** are likely to be introduced at distal positions. In accordance with this, we did not isolate the regioisomer of **2** where the second naphthalene dicarboximide substituent was annulated at the [2,3] or [8,9] positions. Therefore, we deduce that the second boronic ester of **7** is introduced at the 4, 5, 6, or 7 position which in all cases leads to **2** as the sole product.

Scheme 2. Synthesis of Bowl-Shaped Polycyclic Aromatic Bis(dicarboximide) 2[a]



additive	-[b]	-	Bu$_4$NCl	KCl	PivOH
yield of **2** (%)	8	22	31[c]	18	12

[a] Reaction conditions: **7** (1.0 equiv), **5** (3.0 equiv), [Pd$_2$(dba)$_3$]·CHCl$_3$ (20 mol %), P(*o*-tolyl)$_3$ (80 mol %), Cs$_2$CO$_3$ (4.5 equiv), water (100 equiv), *o*-DCB, 90 °C, 2 h then added an additive (1.0 equiv) and 160 °C, 24 h. Yields were determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. [b] Reaction carried out at 160 °C from the beginning (24 h). [c] Isolated yield.

X-ray crystallographic analysis of bowls **1** and **2** gave unequivocal structural assignments and insight into the effects of the number of imide moieties on packing motifs. Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into tetrachloroethane solution of **1** and toluene solution of **2**. The bowl depths of the central corannulene moiety of **1** and **2**, defined as the mean distances between the central five-membered ring and the mean plane of the 10 rim carbons, are 0.92 and 1.00 Å (Figure 2a, b) while that of corannulene is 0.87 Å.[21] This indicates that an increasing number of naphthalene imide moieties leads to a deeper curvature. The crystal structure of **1** consists of columnar stacks of bowls with the shortest contact between two neighboring molecules being 3.16 Å (Figure 2c). Neighboring stacks alternate with respect to the curvature direction of corannulene moieties. We note that columnar stacks of molecules are often seen in reported crystal structures of bowl-shaped PAHs.[12,13,20,24] Each column consists of molecules of **1** that are stacked at the corannulene moiety with naphthalene dicarboximide moieties of each successively stacked molecule offset at an angle of ca. 60° (Figure 2e). The crystal structure of

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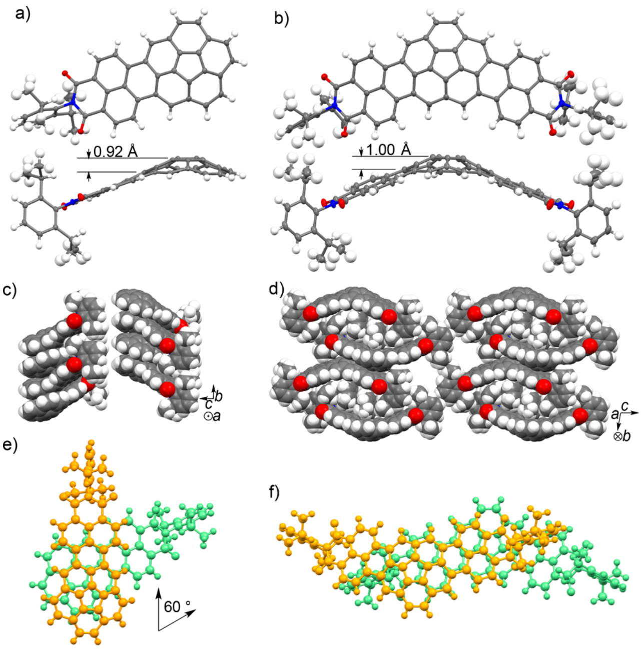

Figure 2. Crystal structures of **1** and **2**. Top and side view of (a) **1** and (b) **2** (ORTEP drawing in 50% probability for thermal ellipsoids). Crystal packing of (c) **1** and (d) **2**. (e) Two stacked molecules of **1** seen from the top side of a columnar stack. (f) A sandwiching pair of **2**. Incorporated solvent molecules are omitted except in (d) where sandwiched toluene molecules are shown (see text).

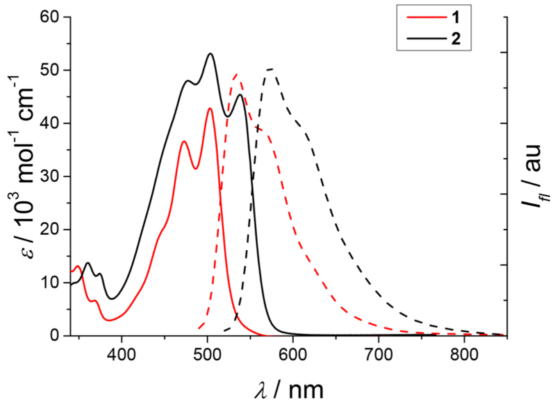

Figure 3. UV−vis absorption (solid line) and fluorescence (dashed line) spectra of **1** (red) and **2** (black) in dichloromethane ($c = 1.0 \times 10^{-5}$ M; 25 °C). λ_{ex} = 473 nm for **1** and 503 nm for **2**.

2 consists of dimers that are sandwiching two toluene solvate molecules (Figure 2d). In each dimer the corannulene moiety is placed over one of the naphthalene dicarboximide arms of the other molecule (Figure 2f). This clamp-like sandwiched packing motif is rare for bowl-shaped PAHs[23,27] and contrasts with the tendency of bowl-shaped molecules to pack into columnar stacks as in the crystal structure of **1**.

These new bowl-shaped molecules resemble planar perylene mono- and bis(dicarboximides) (PMI and PBI). Although PBIs are valued fluorescence dyes with quantum yields close to unity[39] and are outstanding n-type semiconductors,[40] the impact of the corannulene moiety on optical and redox properties is hard to predict. Contrary to the commonly seen insolubility of imide-substituted PAHs, bowls **1** and **2** have high solubility in chlorinated or aromatic solvents owing to their curved π-scaffold (see SI for details). Despite larger π-scaffolds, the solubility of **1** and **2** in chloroform also exceeds that of the PBI derivative with the same bulky imide substituents (9 and 15 vs 6 mg/mL). The optical properties of bowls **1** and **2** were characterized by UV−vis and fluorescence spectroscopy in dichloromethane (Figure 3). The absorption spectra of bowls **1** and **2** reveal S_0−S_1 transition maxima at 503 and 538 nm, respectively, which reflect the extended π-conjugation of **2**. These values are indeed similar to those of their planar congeners PMI (λ_{max} = 510 nm) and PBI (λ_{max} = 526 nm).[39] However, the spectrum of **2** shows a nonprogressional vibronic structure, which stems from overlapping transitions to higher electronic states as revealed by TDDFT calculations (SI). The emission maxima of **1** and **2** appeared at 534 and 573 nm, respectively, from which Stokes shifts were calculated to be 1200 and 1100 cm^{-1}. Such large Stokes shifts are not observed for PMIs and PBIs and resemble those of other reported bowl-shaped PAHs.[41] More importantly, bowls **1** and **2** have high fluorescence quantum yields of 0.55 and 0.48 with lifetimes of 3.18 and 5.00 ns, respectively. Albeit lower than those of PMIs and PBIs, these fluorescence quantum yields are apparently the highest reported for π-conjugated bowl-shaped chromophores.[41] As recently pointed out by Hariharan,[42] core-twisted aromatics suffer from enhanced intersystem crossing and thus the excellent fluorescence properties of **1** and **2** are indeed remarkable.

Electrochemical properties were characterized by cyclic and square wave voltammetry in dichloromethane at room temperature using 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte and the Fc$^+$/Fc redox couple as an internal standard (Figure S1). Bowl **1** showed two reversible reduction processes at −1.38 and −1.67 V, while bowl **2** showed three at −1.22, −1.34, and −1.72 V. Their oxidation processes were observed at 1.10 and 1.14 V. The oxidation and reduction potentials of **1** and **2** are less dependent on the number of imide substituents than those of imide-substituted rylenes.[43,44] Also, all redox potentials are 0.1−0.3 eV higher than those of PMI and PBI,[40] demonstrating the impact of a more electron-rich central unit.

In summary, we synthesized bowl-shaped imide-functionalized PAHs using a recently introduced novel palladium-catalyzed cascade C−C bond formation reaction that comprises Suzuki−Miyaura cross-coupling and direct arylation. This cascade reaction was improved by using a Heck reaction additive, tetrabutylammonium chloride,[35] which is consistent with our recently reported mechanistic rationale.[33] These are the first examples of corannulene annulation with electron-poor aromatic moieties via six-membered ring annulation. The obtained bowl-shaped molecules show exciting functional properties. Despite possessing non-planar π-scaffolds, they are highly luminescent and exhibit low-lying frontier orbitals as desired for acceptors in supramolecular photosystems[45] and n-type semiconductors.[40] Further explorations of the self-assembly behavior of bowl-shaped imide-functionalized PAHs and extensions of our cascade reaction to various substrates are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02618.

Detailed synthetic and experimental procedures, characterization data, NMR spectra, and crystallographic information (PDF)
Crystal data for **1** (CCDC 1569916); Crystal data for **2** (CCDC 1569917) (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: wuerthner@uni-wuerzburg.de.

ORCID

Frank Würthner: 0000-0001-7245-0471

Notes

The authors declare no competing financial interest.

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