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π -Extended Polyaromatic Hydrocarbons by Sustainable Alkyne Annulations through Double C–H/N–H Activation

Elżbieta Gońka,⁺ Long Yang,⁺ Ralf Steinbock, Fabio Pescioli, Rositha Kuniyil and Lutz Ackermann*^[a]

Abstract: The widespread applications of substituted diketopyrrolopyrroles (DPPs) call for the development of efficient methods for their modular assembly. Herein, we present a π -expansion-strategy for polyaromatic hydrocarbons (PAHs) by C–H activation in a sustainable fashion. Thus, twofold C–H/N–H activations were accomplished by versatile ruthenium(II)carboxylate catalysis, providing step-economical access to diversely-decorated fluorogenic DPPs that was merged with late-stage palladium-catalyzed C–H arylation on the thus-assembled DPP motif.

Since their first synthesis,^[1] diketopyrrolopyrroles (DPPs) have attracted great attention of researchers from various research arenas, including optoelectronic material sciences^[2] and bioimaging.^[3] These inconspicuous small organic DPP molecules exhibit versatile properties ranging from low solubility, chemical resistance, outstanding stabilities and distinct colors, which render them excellent pigments.^[4] *N*-Alkylation leads to DPPs with improved solubilities, the properties of which can be fine-tuned by the incorporation of different aromatic motifs.^[3] Due to their strong electron-withdrawing ability and optical properties, DPPs are widely used as small molecules and conjugated semiconducting polymers in organic solar cells (OSCs),^[2a-e, 2g, 5] organic field-effect transistors (OFET),^[2f, 6] organic photovoltaic cells (OPVs),^[7] as well as fluorescent probes,^[3, 8] photocatalysts,^[9] photosensitizers,^[10] or photothermal therapy agents,^[11] promising annihilator molecules,^[12] self-assembled dyes,^[13] and bioconjugated hybrids.^[14]

DPP derivatives with a highly decorated periphery as well as DPP-based polymers are usually obtained via conventional condensation reactions^[4b, 15] or metal-catalyzed cross-coupling reactions with prefunctionalized substrates.^[4a, 8b, 16] In comparison to the elegant efforts devoted to the modification of the DPP periphery *via* direct functionalization or direct arylation polymerization (DARp),^[17] their *de novo* assembly leading to π -extended structures continuous to be underdeveloped, with notable recent progress by Zumbusch^[18] and Würthner.^[13, 19] Another possibility is represented by the introduction of an ethylene bridge between the nitrogen and the aromatic moiety, which leads to significantly π -expanded compounds.^[20] These DPP derivatives possess sharp absorption and emission peaks,

with very high molar absorption coefficients and unique fluorescence quantum yields,^[20b] featuring after further modification two-photon absorption cross-section.^[20a] Very recently, π -extended DPP moieties were incorporated into alternating donor–acceptor copolymers resulting in a variety of low band gap copolymers.^[21] Despite of these indisputable advances, thus far, these DPPs were obtained by classical *N*-alkylation with bromoacetaldehyde diethyl acetal, along with electrophilic aromatic substitution. Notably, this approach is hence limited to the introduction of ethylene junctions with only one substituent.

During the past decade, C–H activation has been identified as a transformative platform for various small molecule derivatizations via alkyne annulations.^[22] In sharp contrast, DPP assembly and diversification by C–H functionalization or DARp have thus far largely proven elusive.^[17] Within our program on sustainable C–H activation,^[23, 24] we hence devised a versatile strategy for the modular assembly of DPPs in a single step by twofold C–H/N–H activation. Salient features of our findings include: 1) innovative ruthenium-catalyzed double C–H/N–H annulation of DPPs, 2) a π -expansion-strategy for PAHs, 3), access to valuable dyes with high absorption coefficients, and 4) transformative late-stage diversification by C–H arylation on the DPP motif.

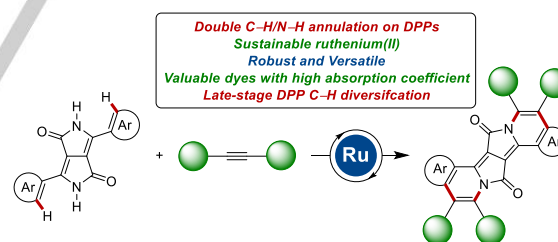


Figure 1. Double C–H/N–H activation for modular assembly of diketopyrrolopyrrole PAHs.

We initiated our studies by probing various reaction conditions for the envisioned double C–H/N–H activation of diketopyrrolopyrrole **1a** with alkyne **2a** (Table 1, for detailed information, see Tables S-1 and S-2 in the Supporting Information).^[25] Thus, moisture- and air-stable ruthenium(II) complexes emerged as the catalysts of choice, with most effective catalysis accomplished by carboxylate assistance (entries 1-4).^[26] Given the rather poor solubility of substrate **1a**^[1, 4b] and the aromatic character of PAH **3aa**, we next explored various solvents (entries 4-9), with *o*-xylene being superior. Control experiments confirmed the essential role of carboxylate-assisted ruthenium(II) catalysis (entries 10-11). The particularly challenging character of

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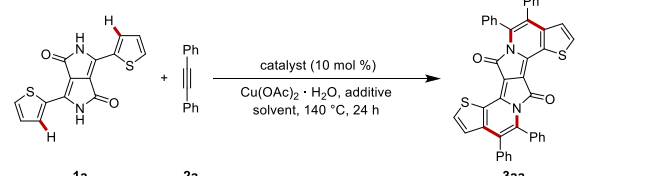
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the twofold C–H/N–H activation was reflected by palladium and iridium catalysts failing short in delivering the desired product **3aa** (entries 13 and 14). Likewise Cp*Rh(III)-catalysis was significantly less effective than the cost-effective ruthenium(II) manifold (entries 15 and 16).

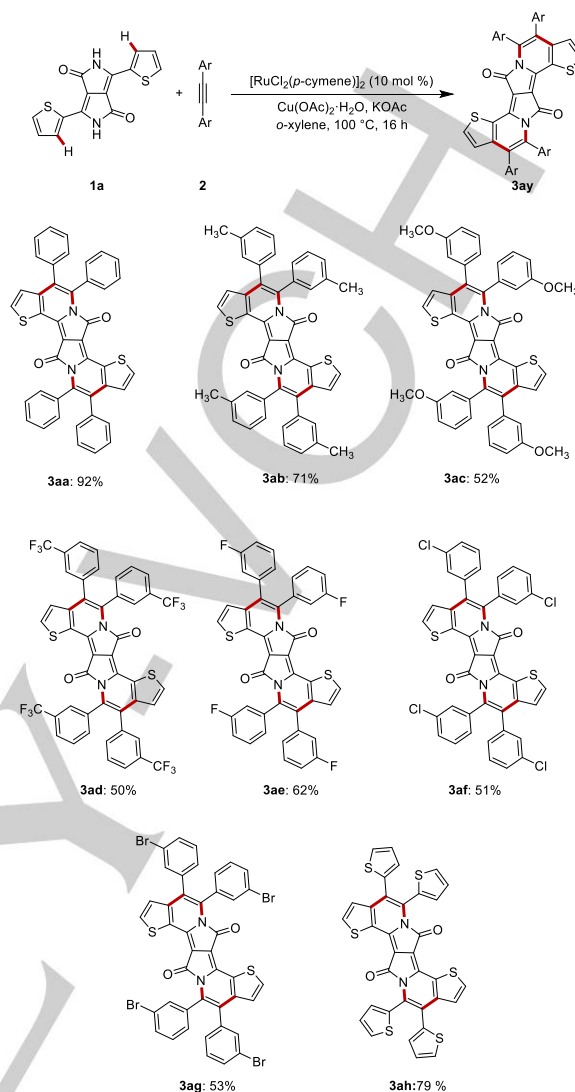
Table 1. Optimization of double C–H/N–H activation on DPP **1a**.^[a]



Entry	Catalyst	Additive	Solvent	Yield ^[b]
1	[RuCl ₂ (<i>p</i> -cymene)] ₂	---	<i>o</i> -xylene	35%
2	[RuCl ₂ (<i>p</i> -cymene)] ₂	KOAc	<i>o</i> -xylene	80%
3 ^[c, d]	[RuCl ₂ (<i>p</i> -cymene)] ₂	KOAc	<i>o</i> -xylene	92%
4 ^[d]	[RuCl ₂ (<i>p</i> -cymene)] ₂	KOAc	<i>o</i> -xylene	84%
5	[RuCl ₂ (<i>p</i> -cymene)] ₂	KOAc	DCE	70%
6	[RuCl ₂ (<i>p</i> -cymene)] ₂	KOAc	PhMe	56%
7	[RuCl ₂ (<i>p</i> -cymene)] ₂	KOAc	<i>t</i> -AmOH	57%
8	[RuCl ₂ (<i>p</i> -cymene)] ₂	KOAc	DMF	---
9	[RuCl ₂ (<i>p</i> -cymene)] ₂	KOAc	GVL	---
10	---	KOAc	<i>o</i> -xylene	---
11 ^[e]	[RuCl ₂ (<i>p</i> -cymene)] ₂	---	<i>o</i> -xylene	---
12 ^[e]	[RuCl ₂ (<i>p</i> -cymene)] ₂	KOAc	<i>o</i> -xylene	---
13 ^[f]	Pd(OAc) ₂	KOAc	<i>o</i> -xylene	---
14	[Cp*IrCl ₂] ₂	KOAc	<i>o</i> -xylene	---
15	[RhCp*Cl ₂] ₂	KOAc	<i>o</i> -xylene	76%
16 ^[c, d]	[RhCp*Cl ₂] ₂	KOAc	<i>o</i> -xylene	20%

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (1.00 mmol), catalyst (10 mol %), Cu(OAc)₂·H₂O (0.5 mmol), additive (0.25 mmol), solvent (0.2 M), 140 °C, 24 h. [b] isolated yields. [c] 16 h. [d] 100 °C. [e] CuBr₂ as an oxidant. [f] 20 mol %.

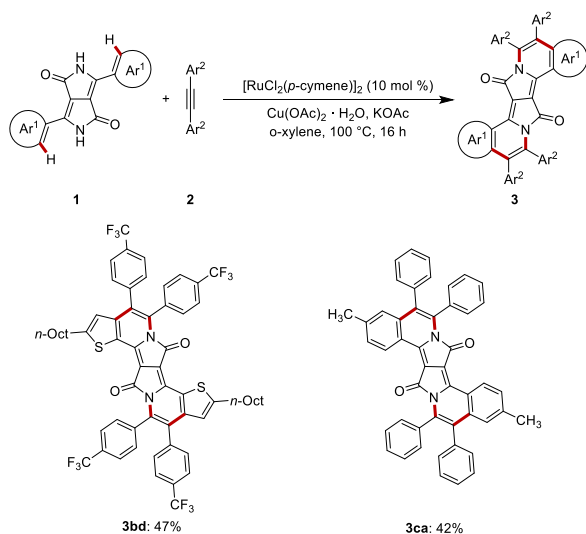
With the optimized catalyst in hand, we tested its versatility in the double C–H/N–H activation of DPP **1a** with a variety of aryl-substituted alkynes **2** (Scheme 1). Thereby, π -extended PAHs were accessed from electron-rich as well as electron-deficient alkynes in an efficient manner, including sensitive tetra-bromo DPP **3ag** and thiophene-rich **3ah**, which should prove instrumental for further modifications and applications of the DPPs **3**.



Scheme 1. Ruthenium(II)-catalyzed double C–H/N–H activation with aryl alkynes **2**.

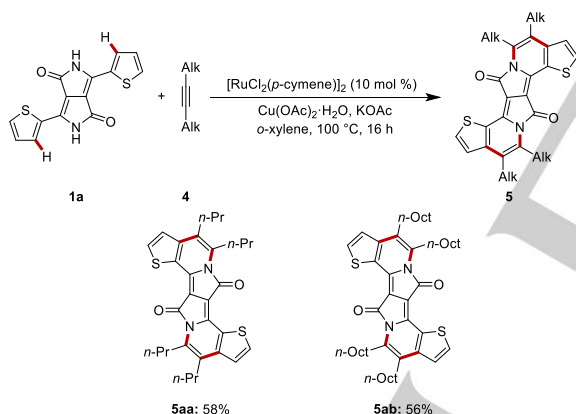
The double ruthenium catalyzed DPP C–H/N–H activation was not restricted to unsubstituted, parent DPP **1a** (Scheme 2). Indeed, the reaction also proceeded efficiently with alkyl-substituted derivative **1b** as well as the aryl-modified-DPP **1c**, with the isolated yield of annulation product **3ca** being caused by the extremely low solubility of substrate **1c**.

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Scheme 2. Double ruthenium-catalyzed C–H/N–H activations of DPPs **1**.

Next, we evaluated alkyl-substituted alkynes **4** in the twofold ruthenium-catalyzed alkyne annulation by DPP **1a** (Scheme 3). Hence, the desired π -extended PAHs **5aa** and **5ab** were obtained by efficient oxidative C–H/N–H activations.



Scheme 3. Twofold annulations of alkyl-alkynes **4** by DPP **1a**.

The connectivity of the annulated product **3aa** was unambiguously established by X-ray crystal diffraction analysis (Figure 2). The dihedral angle between the DPP unit and its adjacent thiophene unit was found with 6.4° , clearly showing the importance of the molecular tether to induce planarity, as compared with the unbridged compound.^[6c] Further, the individual molecules are arranged in a lamellar packing motif,^[27] which appears to be stabilized by dispersive non-covalent C–H \cdots π interaction between the C–H bonds of the arene motif and the thiophene unit (2.82 Å).

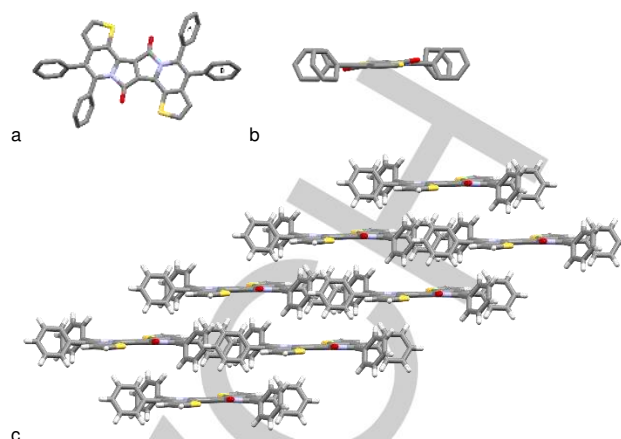


Figure 2. X-Ray structure of DPP **3aa**. a) Molecular structure. b) Side view on the molecular structure, highlighting the planarity of the DPP core. c) Lamellar packing motif. Hydrogen atoms are partially omitted for clarity.

The optical properties of the thus-obtained novel DPP PAHs **3**, **5** and **7** were thereafter studied by detailed UV-Vis absorption and fluorescence spectroscopy (Table 2). The unprecedented DPPs exhibited very intense absorption in the UV and visible region, with absorption maxima between 600 – 640 nm, which results in an intense blue to purple color. The absorption maximum in all synthesized derivatives is bathochromically shifted in comparison with the previously synthesized, unsubstituted compounds,^[20b] whereas both Stoke shift and absorption coefficient are comparable. Interestingly, the highest absorption coefficients were obtained for the *p*-tolyl-DPP derivative **3ca**, while the largest Stokes shift was observed for thiophene-DPP derivative **3aa**.

Table 2. Spectroscopic data of DPPs **3**, **5** and **7**.

compound	$\lambda_{abs,max}$	$\lambda_{em,max}$	Stokes shift [cm^{-1}]	ϵ_{max} [$\text{M}^{-1} \text{cm}^{-1}$]
3aa	633	645	293	78677
3ab	635	645	244	52083
3ac	635	646	268	71946
3ad	632	641	222	66051
3ae	631	640	223	47269
3af	633	644	270	76626
3ag	633	643	246	76107
3ah	636	646	243	25878
3bd	637	644	158	11431
3ca	604	613	270	92095
5aa	630	639	223	71598
5ab	631	642	272	84835
7	680	694	296	53634

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In order to investigate further the electronic structure of the DPPs **3**, we performed computational DFT studies for product **3aa** at the B3LYP-D3(BJ)/6-311+G(d,p)+SMD(o-Xylene) level of theory (Figure 3).^[25] Our calculations showed that the HOMO is delocalized over the DPPs core and the ethylene bridge, whereas the LUMO is evenly localized on all condensed rings. Moreover, our TD-DFT calculations, performed at the same level of theory, highlighted an optical gap (E_{opt}) of 2.02 eV. Our computed absorption spectrum is in good qualitative agreement with the experimental data.^[25]

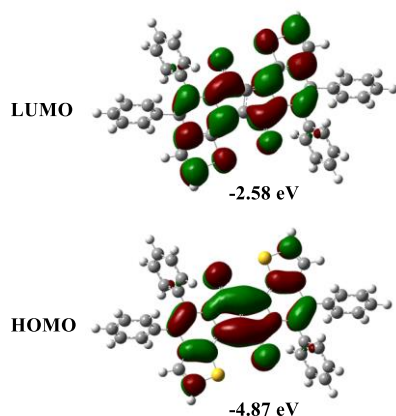
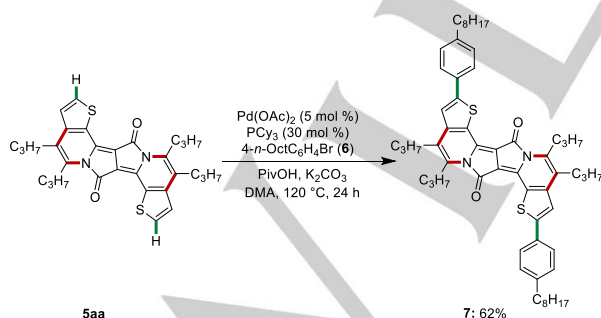


Figure 3. Energies and shapes of frontier orbitals (HOMO and LUMO) of **3aa** calculated at B3LYP-D3(BJ)/6-311+G(d,p)+SMD(o-Xylene) level of theory.

Finally, we became attracted by further late-stage functionalization of PAH **3am** in terms of the introduction of two aryl motifs^[17a] at the alpha positions of the thiophenes (Scheme 4). Thus, the desired assembly of octylphenyl-substituted DPP **7** was realized by palladium-catalyzed twofold C–H arylations. It is noteworthy that the C–H activation-based incorporation of two aromatic moieties drastically shifted both the absorption and the emission maxima into the NIR region, which was mirrored by the green color of PAH **7**.



Scheme 4. Late-stage PAH diversification by double C–H arylations. Cy = cyclohexyl; DMA = dimethylacetamide; PivOH = pivalic acid.

In summary, we have devised an enabling strategy for the assembly of π -extended DPPs. Thus, ruthenium(II)-catalyzed

double C–H/N–H activation allowed for the synthesis of novel, diversely-decorated DPP derivatives in a step-economical manner. The novel DPPs were fully characterized, including spectroscopy, X-ray diffraction and DFT computation. The twofold alkyne annulation was furthermore merged with C–H arylations of the thus obtained π -extended PAHs to furnish DPPs with absorption and emission maxima shifted into the NIR region. Our findings should prove invaluable for applications to optoelectronics, material sciences and live cell imaging.^[28]

Acknowledgements

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Keywords: Annulation • C–H Activation • Diketopyrrolopyrroles • Ruthenium • PAHs

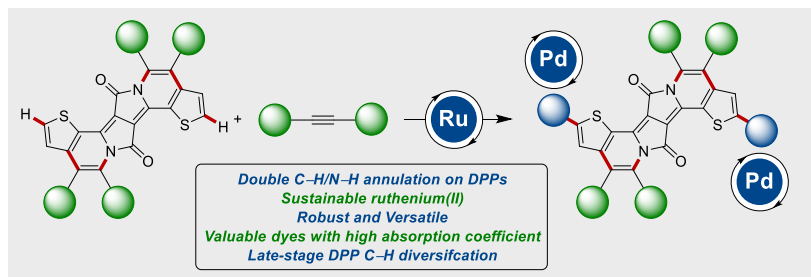
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π -Extended Polyaromatic Hydrocarbons by Sustainable Alkyne Annulations through Double C-H/N-H Activation

PAHs: Double C-H/N-H activation by ruthenium(II) catalysis enabled the assembly of π -expanded diketopyrrolopyrroles with unique spectroscopic features.