Cross-coupling-annulation cascade from peri-dibromonaphthalimide to pseudo-rylene bisimides

Organic Chemistry Frontiers

RESEARCH ARTICLE

Cross-coupling-annulation cascade from *peri*-dibromonaphthalimide to *pseudo*-rylene bisimides†

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Herein we report a synthetic method to annulate naphthalimide moieties at different positions of a pyrene core by a cascade reaction involving palladium-mediated Suzuki-Miyaura cross-coupling and direct C-H arylation affording a new type of rylene bisimides, which we term as *pseudo*-rylene bisimides. The Pd-mediated reactions of *peri*-dibromonaphthalimide and pyrene boronic acid esters lead exclusively to six-membered ring annulations by a cascade C-C bond formation, for which a mechanistic rational is proposed. Depending on the molecular geometry of the new *pseudo*-rylene bisimides, their optical properties resemble those of zethrene or terrylene bisimides, or polycyclic aromatic hydrocarbons like coronenes. The structural integrity of this new type of *pseudo*-rylene bisimides was confirmed by single crystal X-ray analysis.

Introduction

Rylene bisimides are among the most studied classes of π-conjugated dyes during the last decades due to their extraordinary properties such as tuneable intense absorption and emission ranging from ultra-violet to near-infrared spectral region, adjustable frontier molecular orbital energies, reversible reduction processes as well as high thermal and photochemical stability, which enable their application as electron-acceptor materials in (opto)electronic devices.[1] Rylene bisimides consist of fused naphthalene units that are linked via the *peri* positions and bear terminal dicarboximide groups, which exert an electron-withdrawing effect on the aromatic core.[1b, 2] While the lower homologue rylene dyes like naphthalene[3] and perylene bisimides[2b] can be synthesized by imidization of the corresponding bisanhydride precursors, higher rylene bisimides are typically synthesized by cross-coupling reactions of naphthalene and perylene moieties that are prefunctionalized with imide groups followed by intramolecular oxidative coupling under basic conditions.[2a] Furthermore, a lateral core expansion of this class of polycyclic aromatic hydrocarbons (PAHs) is attainable by cross-coupling reactions and C-H arylations.[4] Other dicarboximide-functionalized polycyclic aromatic scaffolds such as anthracene bisimides[5] and decacyclene triimides[6] could be prepared by multiple-step synthesis of the corresponding anhydrides followed by imidization of the anhydrides in the final step. Another highly interesting class of terminally naphthalimide-functionalized PAHs, namely zethrene bisimides, were synthesized by the Wu group through Pd-catalyzed cyclodimerization of respective naphthalimide precursors.[7]

In our endeavor to advance from one- to two-dimensional electron-poor polycyclic π-systems, we have recently reported the synthesis of a C_{64} nanographene bearing four dicarboximide groups at the corners by a new synthetic protocol involving Pd-catalyzed cross-coupling reaction of a dibromonaphthalimide and tetra-substituted pyrene boronic acid pinacol ester.[8] Amazingly, in this one-pot reaction under commonly used Suzuki-Miyaura cross-coupling conditions ten C-C bonds were formed by C-C cross-coupling, C-H arylation and oxidative dehydrogenation to afford this novel π-system. To get more insight into this intriguing reaction, we have now studied more simple systems by using mono- and disubstituted pyrene boronic acid esters and the same dibromo-naphthalimide. Here we report that Pd-catalyzed cross-coupling reactions of the above-mentioned components lead exclusively to six-membered annulation of naphthalimide moieties to the pyrene core affording a new type of rylene bisimides that contain a pyrene, instead of naphthalene as bridging unit, which we name as *pseudo*-rylene bisimides.

Results and discussion

Synthesis and mechanistic rational

The mono- and disubstituted pyrene boronic acid pinacol esters **7**, **8** and **9** were synthesized from the respective brominated derivatives **4**, **5** and **6** by Miyaura borylation[9] with bis(pinacolato)diboron (B_2pin_2) as boronic acid ester source and isolated in high yields of $77 - 83\%$ after chromatographic purification. The precursor *N*-(2,6-diisopropylphenyl)-4,5-di-bromo-1,8-naphthalimide **10** was synthesized in two steps by

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Org. Chem. Front., 2016, **00**, 1-8 | **1**
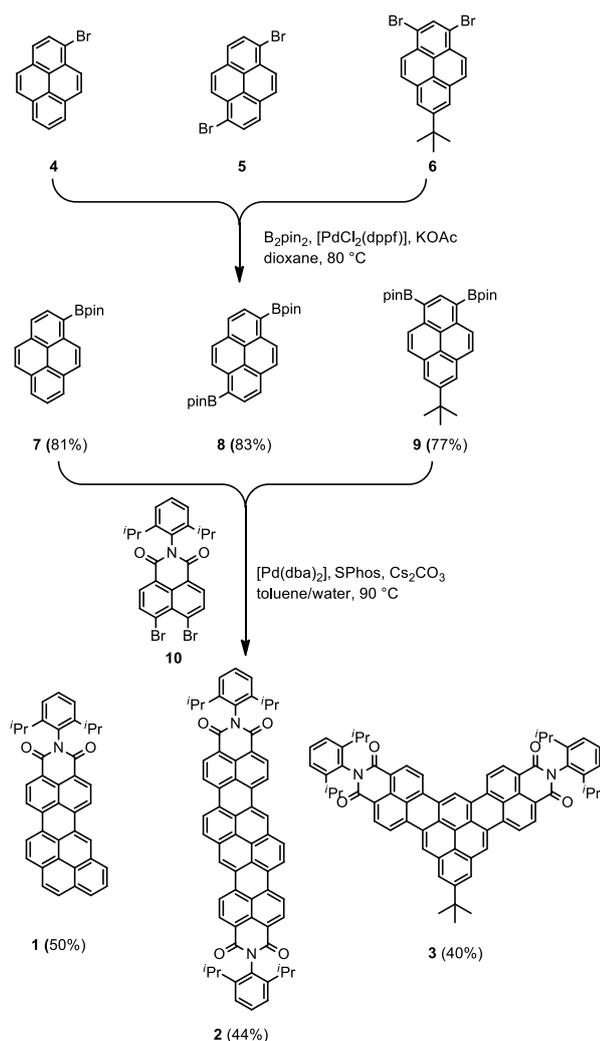
Scheme 1 Synthetic routes to new type of *pseudo*-rylene imide **1** and bisimides **2** and **3** (dppf: 1,1'-bis(diphenylphosphino)ferrocene, dba: dibenzylideneacetone, SPhos: 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl)
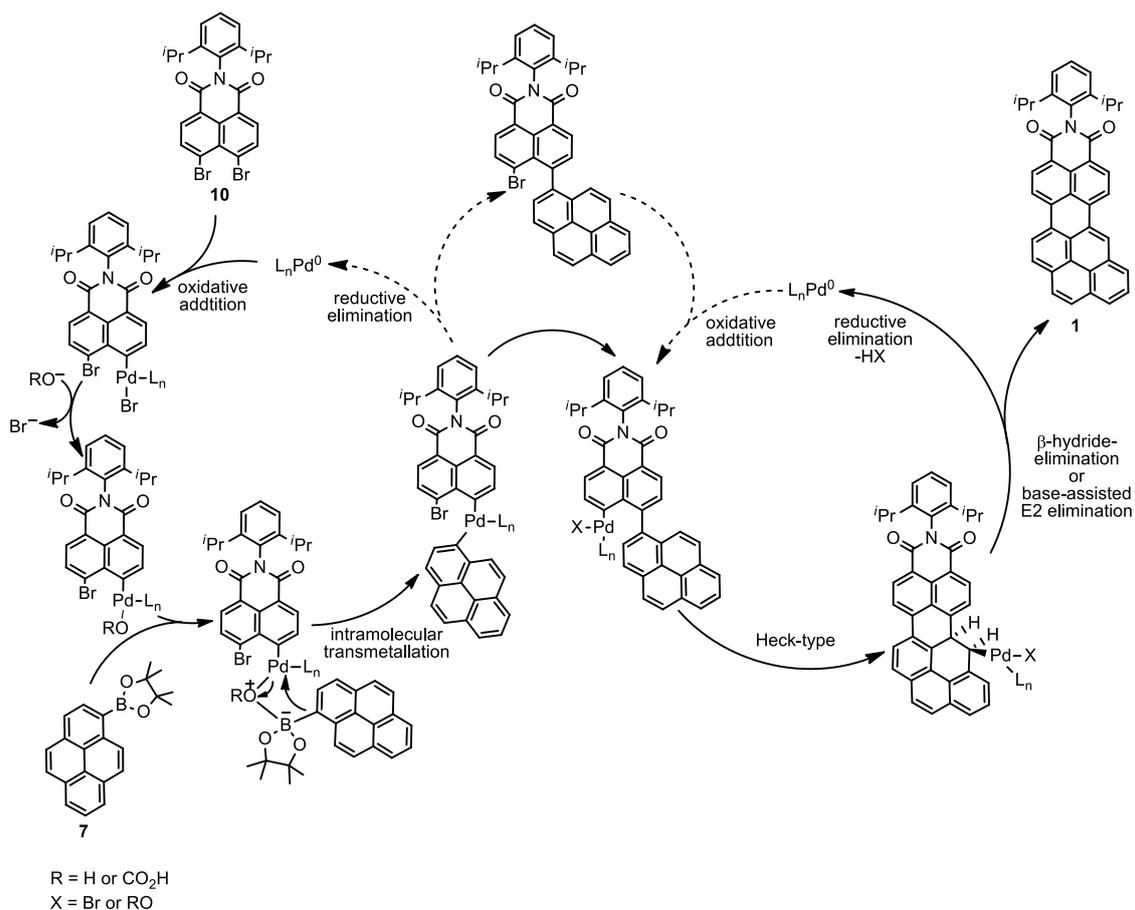
Hunsdiecker reaction of naphthalene bisanhydride[10] and subsequent imidization with 2,6-diisopropylaniline under acidic conditions.[7a] The palladium-catalyzed cross-coupling reaction of dibromonaphthalimide **10** with the particular pyrene boronic acid pinacol esters **7**, **8** and **9** afforded the six-membered ring annulated polycyclic aromatic compounds **1**, **2** and **3**, respectively, in 40 – 50% isolated yields (Scheme 1). Although by this reaction a five-membered ring annulation is in principle possible, such products were not detected.

We have applied typical conditions for Suzuki-Miyaura cross coupling reactions,[11] thus we assume an initial C-C bond formation by Suzuki cross coupling, which might lead to a mono-halogenated intermediate, but was not detected, that can undergo further activation by palladium and rapid direct C-H arylation (Scheme 2). While different mechanisms have been discussed in the literature for direct C-H arylations,[12] we consider a Suzuki-Heck-type coupling cascade to be the most likely pathway for the present case. A plausible mechanistic rational is illustrated in Scheme 2, where the initial C-C coupling takes place via Suzuki-Miyaura cross coupling (left

cycle) and a second C-C bond formation by Pd-catalyzed Heck-type C-H arylation (right cycle). One possible explanation for a favored Heck-type coupling might be that a competing mechanism by electrophilic aromatic substitution (S_EAr) or concerted metalation deprotonation (CMD) would lead to a seven-membered palladacycle intermediate. Such an intermediate would entail a drastic deformation of the aromatic cores and should accordingly be unfavored. Indeed, Rice and co-workers have observed the formation of cyclopenta-fused PAHs by intramolecular coupling of two naphthalene moieties through a six-membered palladacycle intermediate, which is of less steric constraint.[13] However, we could not detect any cyclopenta-fused systems under the reaction conditions applied. Moreover, the possibility of a Heck-type mechanism was proposed for several Pd-catalyzed arylations in the past.[14] As illustrated in Scheme 2 (right cycle) the oxidative addition of the aryl-halide bond to the Pd-center takes place in the first step. Then the halide might be exchanged by another anionic ligand (i.e. OH^- or CO_3H^-), followed by carbo-palladation. In the last step of the catalytic cycle, an *anti*-β-hydride elimination or a base-assisted E2 elimination leads to the cyclohexa-fused product.[14c, 14d] For diboronated pyrenes **8** and **9**, which lead to annulation of two naphthalimide moieties, similar repeating catalytic cycles are anticipated.

Structural elucidation

The new electron-poor PAHs **1**, **2** and **3** were characterized by ^{1}H, ^{13}C NMR spectroscopy and high-resolution mass spectrometry. Furthermore, single crystals of **1** and **2** suitable for X-ray analysis could be grown by slow diffusion of non-polar solvents into their dichloromethane solutions (for details see Electronic Supplementary Information, ESI†) and thus their molecular structures could be unambiguously confirmed (Fig. 1, S3 and S4, ESI†). Due to its comparatively high dipole moment of 7.0 Debye (obtained by DFT calculations), the solid state packing arrangement of **1** (Fig. 1a and S3, ESI†) is characterized by tightly stacked antiparallel dimers with average π-π distances of approximately 3.55 Å and the crystallographic inversion centers are located in the centers of gravity. These dimers are further interconnected by multiple short C-H···O contacts (< sum of van der Waals radii) between adjacent molecules. However, the sterically demanding imide substituents force the individual dimers to be displaced laterally and longitudinally against each other, giving rise to voids that are filled with dichloromethane molecules. In contrast, the centrosymmetric pyrene-bisnaphthalimide conjugate **2** (Fig. 1b and S4, ESI†) exhibits a slipped stacked solid-state packing with intermolecular π-π distances of 6.99 Å and C-H···π as well as C-H···O hydrogen bonding interactions between neighboring molecules. The large π-surfaces of **2** are additionally solvated by two toluene molecules each, whereas the voids between two slipped stacked chromophores are filled with dichloromethane molecules. Both molecules **1** and **2** exhibit almost perfectly planar π-scaffolds with C-C bond length between 1.342 to 1.479 Å (**1**) and 1.368 to 1.474 Å (**2**),

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Org. Chem. Front., 2016, **00**, 1-8 | **2**

Scheme 2 A mechanistic proposal for the Pd-catalyzed cross-coupling-annulation cascade illustrated for the formation of compound **1** as an example

corroborating their polycyclic aromatic character. Interestingly, in both compounds the shortest C-C bonds are located in the 4-5 and 9-10 positions of the central pyrene core. Therefore, these positions have the most olefinic character in the molecule that might influence their reactivity towards additional annulation by the proposed Heck-type mechanism via a Pd-π complex.

Fig. 1 Solid-state molecular structures of compounds **1** (a) and **2** (b) determined by single-crystal X-ray diffraction (top: front view, bottom: side view; solvent molecules are omitted for clarity, ellipsoids set at 50 % probability).

Optical properties

The optical properties of the naphthalimide-annulated scaffolds **1**-**3** were characterized by UV/Vis absorption and emission spectroscopy in dichloromethane at room temperature (Fig. 2 and S1, ESI†). Distinct absorption spectral features are displayed by these π-extended PAHs **1**-**3** with remarkably high molar absorptivities in the visible range (Table 1). Compound **1** exhibits a broad S_0-S_1 absorption band with a maximum at 547 nm (ε = 44200 M^{-1}cm^{-1}) without any well-defined vibronic fine structure, which is shifted about 77 nm to higher wavelength compared to the parent molecule without dicarboximide substituents, i.e. naphtho[8,1,2-*bcd*]perylene (λ_{max} = 470 nm),[15] and about 38 nm compared to the analogous perylene monoimide (**PMI**; λ_{max} = 509 nm, ε = 34700 M^{-1}cm^{-1}).[16] These observations can be attributed to the extension of the π-system by the core structure and the electron-withdrawing effect of the imide substituent. In contrast, the symmetric PAH **2** displays a S_0-S_1 transition with well resolved vibronic progression from aromatic C-C stretching vibrations and an absorption maximum at 663 nm (ε = 152200 M^{-1}cm^{-1}). Compared to its analogue without dicarboximide groups, i.e. dibenzo[*lm,yz*]pyranthrene (λ_{max} = 575 nm),[15] the absorption is again shifted by 88 nm to higher wavelength due to the electron-withdrawing imide groups.
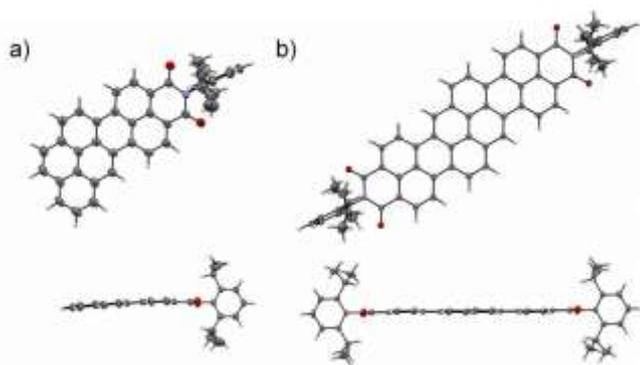
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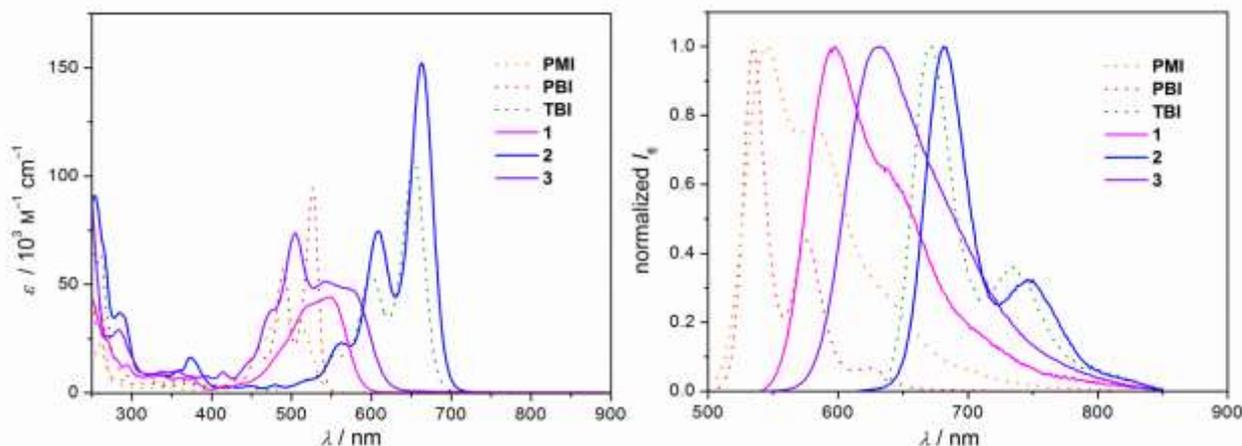*Org. Chem. Front.*, 2016, **00**, 1-8 | **3**

Fig. 2 UV/Vis absorption (left) and emission spectra (right, λ_{ex} = 530 (**1**), 605 (**2**) and 530 nm (**3**)) of compounds **1** (magenta), **2** (blue), **3** (violet), perylene monoimide (**PMI**, orange dotted), perylene bisimide (**PBI**, red dotted) and terrylene bisimide (**TBI**, green dotted) measured in CH_2Cl_2 (c ~ $1 \cdot 10^{-5}$ M) at room temperature. For the structures of **PMI**, **PBI** and **TBI** see Chart 1.

Interestingly, this *pseudo*-rylene bisimide **2** shows a similar spectral shape as terrylene bisimide (**TBI**; λ_{max} = 650 nm)[17] or zethrene bisimide (**ZBI**; λ_{max} = 648 nm)[7c] but the absorption is of higher intensity and red-shifted by 13 and 15 nm, respectively.

The emission spectra of monoimide **1** and bisimide **2** reveal mirror image relationship with their respective absorption spectra with Stokes shifts of 1559 (**1**) and 399 cm^{-1} (**2**) and fluorescence quantum yields of 79 ± 4% (**1**) and 40 ± 5% (**2**). While the quantum yield of **1** is very close to that of perylene monoimide (90%),[16] the quantum yield of **2** is lower than the value of the analogous perylene and terrylene bisimides (100 and 90%) but in the similar range of zethrene bisimide (53%)[7c], implying that the geometry of **2** has an effect on emission properties as compound **2** and zethrene bisimide possess a similar offset of both naphthalimide moieties.

While the optical signatures of **1** and **2** obviously relate to those of core-unsubstituted rylene mono- and bisimides (Table 1),[16-19, 21] which show intense S_0-S_1 transitions, the absorption and emission properties of the angular pseudo-rylene bisimide **3** differ considerably from those of **1** and **2** as a consequence of a different symmetry and V-shape-type conjugation path of the π-scaffold. Therefore, compound **3** exhibits optical transitions not only to the first excited state but also to higher excited states displaying maxima at 504 and 543 nm (ε = 73700 and 51400 M^{-1}cm^{-1}) and a broad shoulder reaching up to 575 nm, similar to several polycyclic aromatic systems like pyrenes[22] or imide-substituted coronenes[23] and our recently reported tetraimide-substituted C_{64} nanographene.[8] These observations are in good agreement with the TD-DFT calculated spectra (Fig. S2, ESI†). According to these calculations, the transition dipole moments of these two main transitions are aligned along the short and long molecular axes of the central pyrene core (Fig. S2, ESI†). Interestingly, bright fluorescence is observed for **3** at 632 nm with a quantum yield of 79 ±5%.
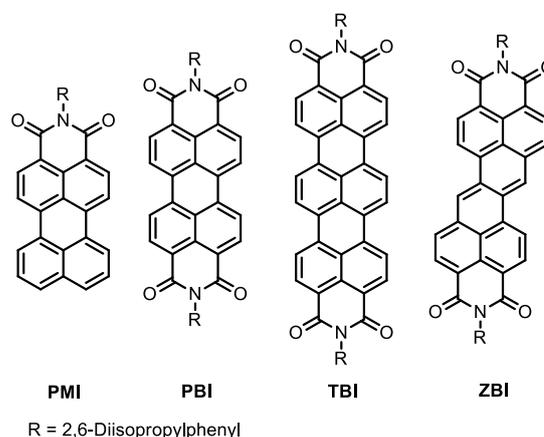

R = 2,6-Diisopropylphenyl

Chart 1 Structures of dicarboximide-functionalized aromatic compounds

Redox properties

To experimentally assess the electronic character of **1**-**3**, cyclic and square wave voltammetry (Fig. 3) was performed. Multiple redox processes are observed for the PAHs **1**-**3**. Thus, compound **1** exhibits two well separated and reversible reduction processes at −1.35 and −1.79 V vs the ferrocenium/ferrocene (Fc$^+$/Fc) redox couple, besides one reversible oxidation at +0.75 V. Compared to a perylene monoimide (−1.46, −1.95 V and +0.95 V)[16] these potentials are shifted to less negative and less positive values, what goes in hand with a smaller HOMO-LUMO gap which is in accordance with the redshift of the absorption spectrum (Fig. 2). Compound **2** bearing two electron-withdrawing naphthalimide subunits can be reduced twice at nearly identical potentials (−1.13 V) that are, however, cathodically shifted by 220 and 660 mV compared to those of **1**. Additionally, one single oxidation at +0.67 V can clearly be observed for **2**, whose integrated current is approximately the half of the anionic reduction. The overlap of both reduction processes can be explained by the larger distance between the two

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Org. Chem. Front., 2016, **00**, 1-8 | **4**

Table 1 Optical and electrochemical data of compounds **1**-**3** and selected dicarboximide functionalized aromatics

Cpd.	λ_{abs} [nm]	λ_{em} [nm]	Ø [%]	E_{ox} [V]	E_{red1} [V]	E_{red2} [V]	$E_{HOMO}{}^{d}$ [eV]	$E_{LUMO}{}^{d}$ [eV]
1	547[a]	598[a]	79 ± 4[a]	0.75[c]	−1.35[c]	−1.79[c]	−5.55	−3.45
2	663[a]	681[a]	40 ± 5[a]	0.67[c]	−1.13*[c]	−1.13*[c]	−5.47	−3.67
3	575[a]	632[a]	79 ± 5[a]	0.73[c]	−1.28[c]	−1.52[c]	−5.53	−3.52
PMI[16]	509[b]	539[b]	90[b]	0.95[c]	−1.46[c]	−1.95[c]	−5.75	−3.24
PBI[18]	526[b]	531[b]	100[b]	1.29[c]	−1.01[c]	−1.24[c]	−6.09	−3.79
TBI[17, 19]	650[b]	668[b]	90 ± 10[b]	0.79[e]	−1.15[§e]	−1.15[§e]	−5.59	−3.65
ZBI[7c]	648[a]	668[a]	53[a]	0.93[c]	−0.84[f]	-0.99[f]	−5.73	−3.96

[a] Measured in dichloromethane at room temperature. [b] In chloroform. [c] Half-wave potentials were determined by cyclic voltammetry measured in dichloromethane (0.1 M TBAHFP) vs. Fc+/Fc. *This reduction is, according to the integration from square wave data, a two-electron process [M/M^{2-}]. [d]Calculated according to literature know procedure using the experimentally determined redox potentials (E_{LUMO} = −[E (M/M$^-$) + 4.8 eV] and E_{HOMO} = −[E (M/M$^+$) + 4.8 eV]) and the energy level of Fc+/Fc with respect to the vacuum level (−4.8 eV).[20] [e] Peak potentials were determined by cyclic voltammetry measured in CHCl₃/MeCN (4:1, v/v) (0.1 M TBAHFP), taking Fc+/Fc as 0.424 V vs SCE.[19] § According to literature, this is a two-electron process [M/M^{2-}]. [f] Half-wave potentials were determined by cyclic voltammetry measured in tetrahydrofuran (0.1 M TBAHFP) vs. Fc+/Fc.
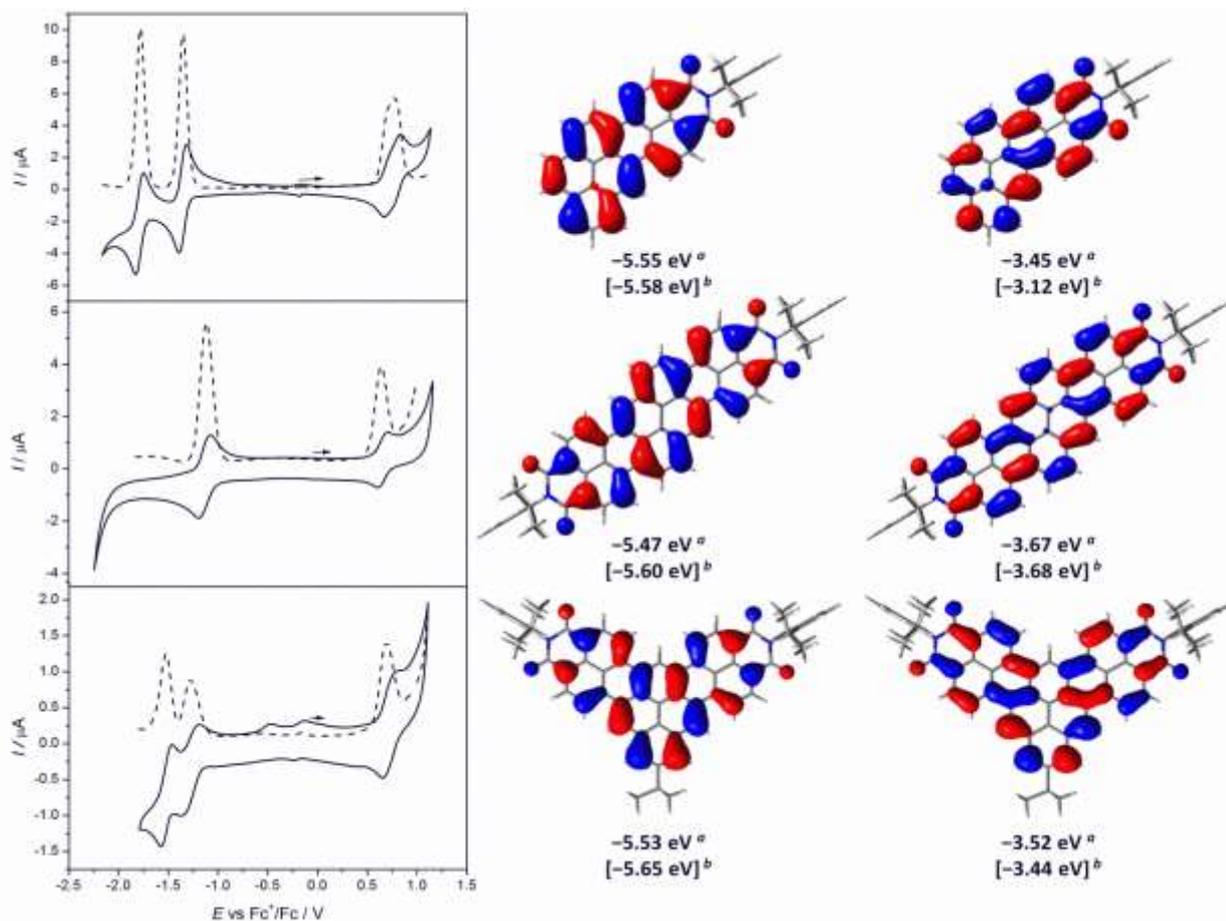

Fig. 3 Cyclic (solid line) and square wave (dashed line) voltammogramms of **1**-**3** in CH₂Cl₂ solutions (0.1 M TBAHFP), scan rate 100 mV/s and calculated HOMOs (left) and LUMOs (right) of compounds **1** (top), **2** (middle) and **3** (bottom) by DFT (B3-LYP, def2-SVP, isoval: 0.02 a.u.). [a] Calculated according to literature known procedure using the experimentally determined redox potentials (E_{LUMO} = −[E (M/M$^-$) + 4.8 eV] and E_{HOMO} = −[E (M/M$^+$) + 4.8 eV]) and the energy level of ferrocenium/ferrocene (Fc+/Fc) with respect to the vacuum level (−4.8 eV).[20] [b] DFT calculated values (B3-LYP, def2-SVP).

naphthalimide moieties, which reduces coulombic repulsion. Similar behavior has also been observed for higher rylene bisimides like terrylene and quarterrylene bisimides,[19] but distinguishes **2** from perylene bisimides.[24] Compound **3**,

however, shows again two separated reduction events at −1.28 and −1.52 V and one oxidation at +0.73 V indicating a slightly smaller HOMO-LUMO gap than that of **1** which is in good agreement with the optical data (Fig. 2). Considering the energy level of ferrocenium/ferrocene (Fc$^+$/Fc) with respect to the vacuum level (−4.8 eV),[20] the HOMO and LUMO energy levels of **1**, **2** and **3** can be estimated using their experimentally determined redox potentials. The values thus obtained are in good agreement with our DFT calculations and range from −3.45 eV (**1**) to −3.52 eV (**3**) and −3.67 eV (**2**) for the LUMO and −5.47 eV (**2**) to −5.53 eV (**3**) and −5.55 eV (**1**) for the HOMO levels (Fig. 3). Comparable LUMO levels were reported for other electron-poor dicarboximide-based systems like unsubstituted perylene bisimides (−3.79 eV),[18] or higher rylene bisimides (−3.65 eV for a terrylene bisimide).[19] Furthermore, the energies of the highest occupied molecular orbitals are in the range of compounds like fluorinated or nitrogen-containing acene derivatives (HOMO: −5.4 to −5.5 eV; LUMO: −3.35 to −3.68 eV),[25] that were successfully used as ambipolar materials in electronic devices. Therefore, we are convinced that derivatives of the newly synthesized dyes **1-3** have potential as electron accepting or ambipolar charge transport materials that should be of interest for (opto)electronic devices.

Conclusions

In summary, we have reported here a new C-C-coupling-annulation cascade consisting of a Suzuki-Miyaura cross coupling and C-H arylation to obtain three electron-poor polycyclic aromatic π-systems based on core-expanded pyrenes with dicarboximide substituents attached at different positions. X-ray analysis revealed a planar geometry of the new π-scaffolds. The optical properties are comparable to rylene mono- and bisimides if the core is extended in only one direction of the parent pyrene core. In the case of angular core annulation leading to a V-shaped π-system, absorption to higher excited states also takes place as the overall geometry of the molecule changes and transitions to higher excited states become allowed. Redox properties reveal the potential of the new dicarboximide-functionalized PAHs as electron-accepting materials as they show similar LUMO energies as hitherto extensively studied rylene bisimides. Furthermore, the newly synthesized core-expanded pyrenes might also have the potential to be used as ambipolar charge-transport materials as it was shown by computations from Chen and Chao[26] that the attachment of two naphthalene moieties to a pyrene core at 1,4 and 3,10 positions can reduce the internal reorganization energy for electron and hole transport. Therefore, the present synthetic strategy, allowing the annulation of (multiple) naphthalimide groups to a polycyclic aromatic core of choice in different positions, will pave the way to develop new types of electron-poor dicarboximide-functionalized nanographene scaffolds.

Experimental

General

Chemicals, reagents and solvents were purchased from commercial suppliers. Column chromatography was performed on silica gel (particle size 0.040–0.063 mm) with freshly distilled solvents as eluents. All other commercially available reagents and solvents were of reagent grade and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DMX 400 or a Bruker DMX 600 spectrometer. ^{13}C NMR spectra are broad band proton decoupled. Chemical shifts (δ) are listed in parts per million (ppm) and are reported relative to tetramethylsilane (TMS). Coupling constants (J) are quoted in Hertz (Hz). Spectra are referenced internally to residual proton solvent resonances or natural abundance carbon resonances. High resolution ESI-TOF mass spectrometry was carried out on a microTOF focus instrument (Bruker Daltronik GmbH).

UV/Vis absorption and emission spectroscopy. All measurements were conducted with spectroscopic grade solvents. UV/Vis absorption spectra were recorded on a Perkin Elmer Lamda 35 spectrometer. Steady-state and time-dependent fluorescence spectra were recorded on a PTI QM4-2003 fluorescence spectrometer. Relative fluorescence quantum yields were measured by optical dilute method (A<0.05)[27] by using rhodamine 101 ($\varnothing_{fl}$ = 91.5% in ethanol) or oxazine 1 ($\varnothing_{fl}$ = 15% in ethanol) as reference.[28]

Cyclic voltammetry. For cyclic and square wave voltammetry, a standard commercial electrochemical analyzer (EC epsilon; BAS Instruments, UK) with a three-electrode single-compartment cell was used. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) was purified by recrystallization from ethanol/water and dried under vacuum. The solvent was dried and degassed prior to use. All measurements were performed under argon atmosphere. The measurements were carried out using ferrocenium/ferrocene (Fc$^+$/Fc) as an internal standard for the calibration of the potential. A Pt disc and a Pt wire were used as working and auxiliary electrodes, respectively, and a Ag/AgCl reference electrode was used.

Synthetic procedures and characterization data

1,6-Dibromopyrene (**6**)[29] and *N*-(2,6-diisopropylphenyl)-4,5-dibromo-1,8-naphthalimide (**10**)[7a] were synthesized according to literature procedures.

General procedure for the synthesis of pyrene boronic acid pinacol esters. Brominated pyrenes **4**, **5** and **6** (1.0 equiv.) and bis(pinacolato)diboron (2.0 equiv. for **4** and 3.0 equiv. for **5** and **6**) were suspended in 20 mL of degassed dioxane under nitrogen atmosphere. Then [PdCl$_2$(dppf)] (15%) and KOAc (2.0 equiv. for **4** and 3.0 equiv. for **5** and **6**) were added and the mixture was heated to 80 °C for 20 to 23 h. After being cooled down to room temperature, the solution was filtered through a short pad of silica and washed with dichloromethane. The filtrate was concentrated under reduced pressure and the crude products were purified by column chromatography (silica gel, gradient of

dichloromethane/hexane 1/1 to 3/1) to give the pyrene boronic acid esters **7**, **8** and **9** as colorless solids.

Compound **7**: Yield: 81%. The analytical data correspond to those reported in the literature.[30]

Compound **8**: Yield: 83%. The analytical data correspond to those reported in the literature.[31]

Compound **9**: Yield: 77%. The analytical data correspond to those reported in the literature.[32]

Compound 1. Mono-substituted pyrene boronic acid pinacol ester **7** (57.8 mg, 176 µmol, 1.0 equiv.), *N*-(2,6-diisopropylphenyl)-4,5-dibromo-1,8-naphthalimide **10** (100 mg, 194 µmol, 1.1 equiv.), 51 mg (88 µmol, 0.5 equiv.) bis(dibenzylideneacetone)palladium(0) ([Pd(dba)$_2$]) and 72 mg (176 µmol, 1.0 equiv.) 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos) were dissolved in 6 mL degassed toluene. Subsequently, a solution of 172 mg (528 µmol, 3.0 equiv.) Cs$_2$CO$_3$ in 1 mL of water was added to the reaction mixture and the latter was heated to 90 °C for 17 h. After being cooled down to room temperature, the solution was extracted three times with each 20 mL of dichloromethane after adding 10 mL of water and the combined organic layers were washed with water. The organic solution was dried over MgSO$_4$ and concentrated under vacuum. The crude product was purified by column chromatography (silica gel, gradient of hexane/dichloromethane from 3:2 to 100% dichloromethane), concentrated under vacuum and washed further with methanol to yield *pseudo*-rylene imide **1** (54 mg, 97 µmol, 50%) as a dark-purple solid. Mp.: > 350 °C. UV/vis (CH$_2$Cl$_2$, c ~ 10^{-5} M): λ_{max}/nm 547 (ε/M^{-1}cm^{-1} 44200). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 9.09 (s, 1 H), 8.87 (d, *J* = 8.4 Hz, 1 H), 8.73 (m, 3 H), 8.58 (d, *J* = 8.2 Hz, 1 H), 8.32 (t, *J* = 8.2 Hz, 2 H), 8.26 (d, *J* = 7.4 Hz, 1 H), 8.14 (m, 2 H), 8.06 (t, *J* = 7.6 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 7.36 (d, *J* = 7.7 Hz, 2 H), 2.82 (sep, *J* = 6.8 Hz, 2 H), 1.21 (2xd, *J* = 6.8 Hz, 12 H). ^{13}C NMR (CDCl$_3$, 151 MHz) δ 164.2, 145.9, 138.1, 137.6, 132.8, 132.5, 131.8, 131.5, 131.3, 131.1, 130.9, 129.6, 128.7, 128.4, 128.0, 127.8, 127.7, 127.3, 127.1, 126.8, 126.4, 126.0, 125.2, 125.0, 124.3, 124.2, 122.4, 121.3, 120.8, 120.7, 120.5, 29.3, 24.2. MS HR (ESI-TOF, positive mode, acetonitrile/chloroform) *m/z* calcd for C$_{40}$H$_{29}$NO$_2$ [M]$^+$ 555.21983, found 555.21891.

Compound 2. 1,6-Disubstituted pyrene boronic acid pinacol ester **8** (80.1 mg, 176 µmol, 1.0 equiv.), *N*-(2,6-diisopropylphenyl)-4,5-dibromo-1,8-naphthalimide **10** (200 mg, 388 µmol, 2.2 equiv.), 101 mg (176 µmol, 1.0 equiv.) [Pd(dba)$_2$] and 145 mg (352 µmol, 2.0 equiv.) SPhos were dissolved in 12 mL degassed toluene. Subsequently, a solution of 172 mg (528 µmol, 3.0 equiv.) Cs$_2$CO$_3$ in 2 mL of water was added to the reaction mixture and the latter was heated to 90 °C for 19 h. After cooling down to room temperature, the solution was extracted three times with each 30 mL of dichloromethane after adding 10 mL of water and the combined organic layers were washed with water. The organic solution was dried over MgSO$_4$ and concentrated under vacuum. The crude product was purified by column chromatography (silica gel, gradient of dichloromethane to dichloromethane/1% methanol), followed by washing with methanol and subsequent size exclusion chromatography on bio beads SX3 (dichloromethane/methanol 9:1). The isolated solid was dissolved in chloroform and precipitated by addition of hexane, filtrated and dried in vacuum at 50 °C to yield *pseudo*-rylene bisimide **2** (70 mg, 77 µmol, 44%) as a dark-blue

solid. Mp.: > 350 °C. UV/vis (CH$_2$Cl$_2$, c ~ 10^{-5} M): λ_{max}/nm 563 (ε/M^{-1}cm^{-1} 23000), 608 (74600), 663 (152200). ^{1}H NMR (CDCl$_3$, 600 MHz) δ 9.22 (s, 2 H), 9.00 (d, *J* = 8.8 Hz, 2 H), 8.89 (d, *J* = 8.2 Hz, 2 H), 8.83 (d, *J* = 7.9 Hz, 2 H), 8.80 (d, *J* = 7.9 Hz, 2 H), 8.72 (d, *J* = 8.3 Hz, 2 H), 8.52 (d, *J* = 8.5 Hz, 2 H), 7.51 (t, *J* = 7.9 Hz, 2 H), 7.38 (d, *J* = 7.9 Hz, 4 H), 2.81 (sep, *J* = 6.8 Hz, 4 H), 1.21 (2xd, *J* = 6.8 Hz, 24 H). ^{13}C NMR (CDCl$_3$, 151 MHz) δ 164.1, 164.0, 145.8, 137.2, 136.8, 132.6, 132.0, 131.1, 130.9, 129.7, 129.5, 129.0, 128.9, 127.7, 127.1, 126.3, 125.6, 125.5, 124.3, 124.2, 123.8, 122.0, 121.7, 121.6, 29.9, 29.4, 24.2. MS HR (ESI-TOF, positive mode, acetonitrile/chloroform) *m/z* calcd for C$_{64}$H$_{48}$N$_2$NaO$_4$ [M+Na]$^+$ 931.35063, found 931.35345.

Compound 3. 1,3-Disubstituted pyrene boronic acid pinacol ester **9** (200 mg, 392 µmol, 1.0 equiv.), *N*-(2,6-diisopropylphenyl)-4,5-dibromo-1,8-naphthalimide **10** (444 mg, 862 µmol, 2.2 equiv.), 225 mg (392 µmol, 1.0 equiv.) [Pd(dba)$_2$] and 322 mg (784 µmol, 2.0 equiv.) SPhos were dissolved in 24 mL degassed toluene. Subsequently, a solution of 385 mg (1.18 mmol, 3.0 equiv.) Cs$_2$CO$_3$ in 6 mL of water was added to the reaction mixture and the latter was heated to 90 °C for 19 h. After being cooled down to room temperature, the solution was extracted three times with each 40 mL of dichloromethane after adding 20 mL of water and the combined organic layers were washed with water. The organic solution was dried over MgSO$_4$ and concentrated under vacuum. The crude product was purified by column chromatography (silica gel, gradient of dichloromethane to dichloromethane/1% methanol), followed by washing with methanol and subsequent size exclusion chromatography on bio beads SX3 (dichloromethane/methanol 9:1). The isolated solid was dissolved in chloroform, precipitated by addition of methanol, filtrated and dried in vacuum at 50 °C to yield *pseudo*-rylene bisimide **3** (153 mg, 159 µmol, 40%) as a dark-purple solid. Mp.: > 350 °C. UV/vis (CH$_2$Cl$_2$, c ~ 10^{-5} M): λ_{max}/nm 504 (ε/M^{-1}cm^{-1} 73700), 543 (51400), 575sh (47700). ^{1}H NMR (C$_2$D$_2$Cl$_4$, 600 MHz, 345 K) δ 9.68 (s, 1 H), 9.08 (s, 2 H), 8.69-8.76 (m, 8 H), 8.43 (s, 2 H), 7.43 (t, *J* = 8.0 Hz, 2 H), 7.29 (d, *J* = 7.9 Hz, 4 H), 2.76 (sep, *J* = 6.8 Hz, 4 H), 1.65 (s, 9 H), 1.17 (d, *J* = 6.8 Hz, 24 H). ^{13}C NMR (C$_2$D$_2$Cl$_4$, 151 MHz, 345 K) δ 164.0, 152.5, 146.1, 137.3, 132.4, 132.0, 131.7, 131.6, 130.9, 129.5, 128.9, 127.9, 127.7, 127.5, 127.3, 126.8, 126.2, 124.2, 124.0, 123.9, 122.1, 121.6, 121.1, 120.6, 118.2, 99.9, 35.7, 31.9, 29.5, 24.3. MS HR (ESI-TOF, positive mode, acetonitrile/chloroform) *m/z* calcd for C$_{68}$H$_{56}$N$_2$NaO$_4$ [M+Na]$^+$ 987.41323, found 987.41354.

Acknowledgements

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Org. Chem. Front., 2016, **00**, 1-8 | **8**