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2,5,8,11-Tetraboronic Ester Perylenediimides: A Next Generation Building Block for Dye-Stuff Synthesis

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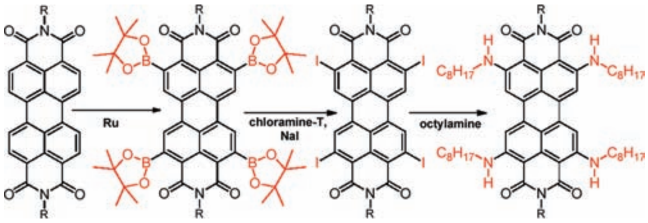
ABSTRACT



Via an unprecedentedly reported ruthenium catalyzed reaction, an efficient and straightforward method was developed for the synthesis of 2,5,8,11-tetraboronate perylenediimide derivatives. A possible reaction mechanism is proposed. The synthesis of 2,5,8,11-tetra-iodo and tetra-amino perylenediimides derivatives is also reported.

Perylenediimides (PDIs) are key chromophores in dye stuff and pigment chemistry. Due to their thermal, chemical, and photochemical stability as well as their excellent optical and electronic properties, they not only serve as industrial colorants[1] but also find applications in organic field effect transistors,[2] photovoltaic devices,[3] and single molecule spectroscopy.[4]

Since the first member of the family was discovered in 1913,[5] PDIs have become one of the most important heterocyclic pigments. In 1959 their potential as highly fluorescent dyes was understood,[6] but a more elaborate chemistry could be developed only during the 1980s, after the discovery of two successful solubilizing strategies developed by Langhals[7] and BASF.[8] The first one relies upon bulky substituents at the imidic nitrogen with the possibility to modulate solubility, with no geometrical modification of the core and alteration of the optical and electronic properties. The second implies the functionalization of the 1,6,7,12-positions (*bay*-positions) via halogenation and successive straightforward nucleophilic substitution[9] or coupling reaction.[10] Solubility, optical, and electronic properties can be finely tailored as desired. However, a geometric distortion of the aromatic core is associated, dependent on the number and nature of the substituents, with consequences on the solid state properties such as self-assembling ability and solid state fluorescence.[11]

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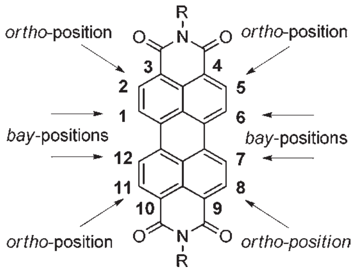


Figure 1. Perylenediimide.

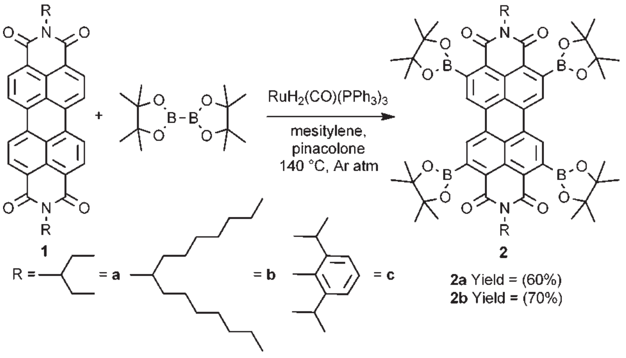
In 2009 a successful method for the selective functionalization of the 2,5,8,11-positions of PDI (defined as *ortho*-positions, Figure 1) was developed.[12] Via ruthenium catalyzed reactions between perylenediimides and terminal alkenes or arylboronates it becomes possible to obtain regioselectively tetraalkylated or tetraarylated PDIs; optical and electronic properties can be successfully tuned without loss of the perylene core planarity. Enhanced solubility and higher solid state fluorescence compared to the unsubstituted parent compounds were demonstrated.[13] Further, alkylation of the *ortho* positions suppresses intermolecular aggregation as well as the formation of intermolecular excited states between PDI molecules, yielding an unprecedented photovoltaic power efficiency of polythiophene:PDI blends.[14]

Nevertheless the synthetic method for the decoration of the 2,5,8,11-positions still presents major disadvantages: (1) the number of terminal alkenes and aryl boronates that can be used in these reactions remains limited; olefins with allylic hydrogens for example undergo rapid isomerization and consequently give lower reaction yields[15] whereas the arylation procedure works in high yields with aryl neopentylglycol boronates, but not as efficiently with other substituents on the boron atom;[16] (2) further limitations arise from the ruthenium complex reactivity: in fact the Murai catalyst ($RuH_2(CO)(PPh_3)_3$) is involved in other catalytic reactions, such as the conversion of nitroarenes into tertiary amines,[17] the rearrangement of oximes into amides,[18] transfer hydrogenation processes,[19] and many others;[20] thus a consistent number of functional groups, such as for example the already cited nitroarenes, internal triple bonds, alcohols, and enones, must be avoided to prevent side reactions; (3) even though the *ortho*-functionalization of PDIs proves the possibility of choice to address the 2,5,8,11-positions selectively, until now only the formation of C−C bonds was demonstrated.

To overcome these problems in our group we developed a facile and straightforward synthesis of 2,5,8,11-tetraboronate PDIs, suitable building blocks for an extension of the chemistry of the *ortho*-positions. The accessibility of these sites is obtained, as in the previously reported alkylation and arylation reactions of PDIs, using the Murai catalyst. At the same time these systems were also synthesized by the group of Shinokubo via an iridium catalyzed borylation reaction.[21]

A PDI and bis(pinacolato)diboron are mixed together and dissolved in a mesitylene/pinacolone mixture. The ruthenium catalyst is added to the reaction, and after heating for 30 h at 140 °C the desired product is obtained and isolated after chromatographic purification. This procedure is applied to PDIs **1a**, **1b**, and **1c**. As already reported in literature,[12] the ruthenium catalyzed 2,5,8,11-functionalization proceeds with higher yields in the presence of sterically less demanding imide substituents, as in the case of compounds **a** and **b** (60% and 70% yield, respectively, Scheme 1). In the case of **c**, the desired tetraboronate is formed in lower yields and cannot be isolated from the mixture of mono-, bi-, and trisubstituted PDI.

Scheme 1. Ruthenium Catalyzed Borylation of PDIs



The proposed reaction mechanism is presented in Scheme 2, and it is similar to the one reported by Kakiuchi and Chatani for the ruthenium catalyzed arylation of aromatic ketones.[16] Also in this case, to increase reaction yields, pinacolone is used as a cosolvent to act as a scavenger of

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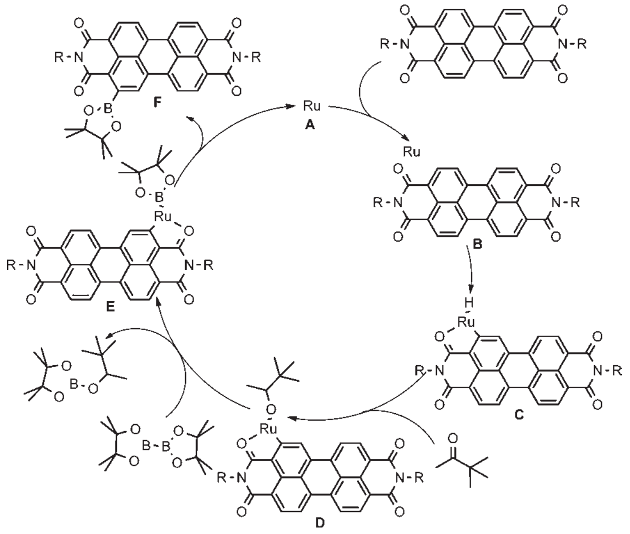
Scheme 2. Proposed Reaction Pathway[a]



[a] Reaction starts with the coordination of the carbonyl by the ruthenium(0) complex **A** to give intermediate **B**, followed by the formation of the *ortho* metalated intermediate **C**, after C–H bond cleavage. Addition of the Ru–H to the carbonyl group of pinacolone leads to the production of the (alkoxy)-ruthenium intermediate **D**. Transmetalation between the bis(pinacolato)diboron and the intermediate **D** results in the formation of a trialkoxyborane and the aryl-boryl-ruthenium complex **E**. Reductive elimination leading to C–B bond formation provides the borylated product **F** and the regeneration of the active catalyst species **A**.

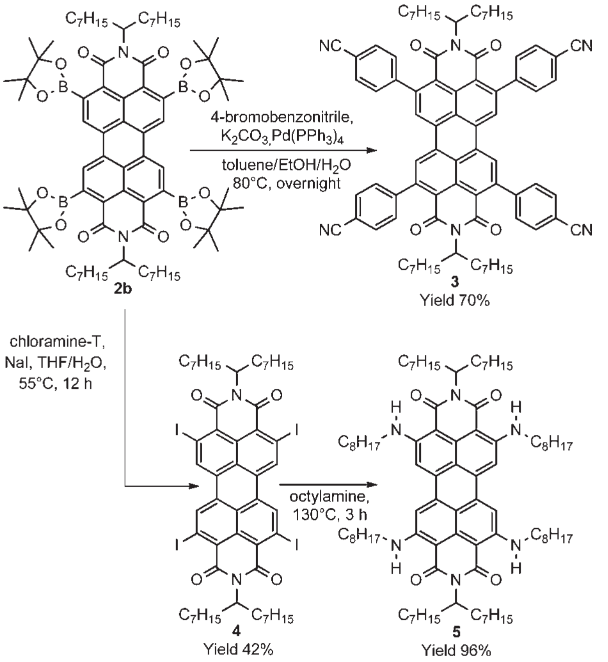
the H–B species and avoid the undesired reduction of the imide group. It is worth noting that, according to the arylation protocol, the aryl boronate **F** should react with another PDI molecule to form a PDI-dimer, but it has not been observed. We believe the reason to be not sterical but instead dependent on the nature of the boronate, deactivated by the strongly electron-withdrawing aryl system and consequently not available for the addition reaction.

To fully elucidate the structural features of 2,5,8,11-tetraboronate PDIs, crystals of compound **2a** were grown from a chloroform/hexane mixture and characterized by X-ray analysis (Supporting Informations, CCDC 823706). As also reported by the group of Shinokubo,[21] the core maintains its planarity, while the sterically demanding boronyl moieties strongly deviate from the plane of the perylene unit.

To prove that the previously mentioned limitations in the synthesis of *ortho*-tetrasubstituted PDIs can be overcomed by using tetraboronate PDIs as intermediates further reactions were performed.

The synthesis of derivative **3** was previously attempted following the ruthenium catalyzed arylation method, but it could not be obtained. Via Suzuki coupling of compound **2b** with 4-bromobenzonitrile the desired tetrasubstitued product could be easily synthesized (70% yield, Scheme 3), isolated, and fully characterized.

Scheme 3. 2,5,8,11-Tetraboronate-PDI as a Building Block



Additionally, the replacement of the boronate groups into iodine atoms was explored. To do so, chloramine-T and sodium iodide in a THF/water mixture were used.[22] The desired iodinated product could be obtained and isolated. With compound **4** being a building block itself, the nucleophilic replacement reaction using octylamine was tested. Similarly to the amination reaction reported in literature for naphthalene diimides,[23] after heating the tetraiodo derivative **4** at 130 °C under an argon atmosphere, full conversion into compound **5** was observed.

Table 1. Optical and Electronic Properties of Reported PDIs

PDI[a]	ε $[M^{-1}cm^{-1}]$[b]	λ_{max} [nm]	λ_{em} [nm][c]	φ_f[d]	E_{red1} [V][e]	LUMO [eV][f]	HOMO [eV][g]
1a	84 300	526	538	0.99	−0.95	−3.85	−6.13
2a	73 000	538	548	0.89	−0.96	−3.84	−6.07
1b	83 300	526	538	0.97	−0.95	−3.85	−6.13
2b	72 100	538	548	0.83	−0.97	−3.83	−6.06
3	62 900	528	542	0.69	−0.90	−3.90	−6.16
4	72 300	518	–	–	−0.89	−3.91	−6.21
5	54 200	512	608	0.05	−1.59	−3.21	−5.61[h]

[a] Optical properties measured in toluene for compounds **1a**, **1b**, **2a**, and **2b**, in dichloromethane for compounds **3**, **4**, and **5**. [b] Measured at λ_{max}. [c] Excited at λ_{max}. [d] Determined using Rhodamine 6G in ethanol as standard. [e] Half-wave potentials, determined by cyclic voltammetric measurement in 0.1 M solution of Bu_4NPF_6 in CH_2Cl_2: vs Fc/Fc$^+$. [f] Estimated vs vacuum level from E_{LUMO} = −4.80 eV − E_{red1}. [g] Estimated from HOMO = LUMO − E_g, where E_g = optical gap, calculated from the optical absorption/emission data. [h] Estimated vs vacuum level from E_{LUMO} = −4.80 eV + E_{ox1}.

All the compounds **2**, **3**, **4**, and **5**, as well as their precursors **1a** and **1b**, were characterized by cyclic voltammetry, UV–visible optical absorption spectroscopy, and

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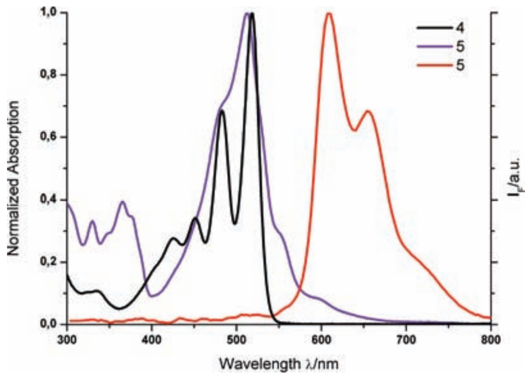

Figure 2. Normalized UV−visible absorption spectra of compounds **4** (black) and **5** (violet) and fluorescence spectra (red) of compound **5** in dichloromethane (λ_{exc} = 512 nm).

photoluminescence spectroscopy (Table 1). It is possible to note that the introduction of four alkylamine moieties in the 2,5,8,11-positions of the perylene core broadens the absorption (Figure 2) but does not cause a strong color change as in the case of tetra-amino-substituted naphthalenediimides.[23] Additionally the introduction of four iodine atoms causes a complete quenching of the fluorescence, due to the heavy atom effect.

As expected, the information obtained by electrochemical investigation shows that the introduction of alkylamine moieties and iodine atoms in the *ortho*-positions of the perylene core causes opposite effects on the HOMO and LUMO energies; in the first case, a consistent lifting is observed (0.64 eV for the LUMO and 0.52 for the HOMO), while for compound **4** only a lowering of less than 0.1 eV occurs.

To conclude we have developed an efficient and straightforward method for the synthesis of 2,5,8,11-tetraboronate PDIs. The potential of these derivatives for the further development of the chemistry of the *ortho*-positions was successfully demonstrated. Additionally replacement of the boronate groups with iodine atoms could be achieved, demonstrating for the first time the possibility to selectively introduce halogen atoms in the 2,5,8,11-positions.

We expect that, due to the broad chemistry of boronic esters, tetraboronate perylendiimides represent the next generation of building blocks for the development of a complete chemistry of the *ortho*-positions of PDIs and the obtainment of new advanced functional materials. Additionally the possibility to selectively form C−B bonds in the *ortho*-position of carboxylic derivatives via ruthenium catalyzed reaction was demonstrated. Studies to fully understand the mechanism of the borylation reaction and its applications are still ongoing in our laboratories.

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Supporting Information Available. Full experimental details and characterization data. CIF file for the X-ray analysis of **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.