# Diborylenetetraaminoperylenes (DIBOTAP): a new class of highly fluorescent functional polycyclic aromatic hydrocarbons with N–B–N units†

**Till Riehm,[a] Gabriele De Paoli,[b] Hubert Wadepohl,[a] Luisa De Cola[b] and Lutz H. Gade*[a]**

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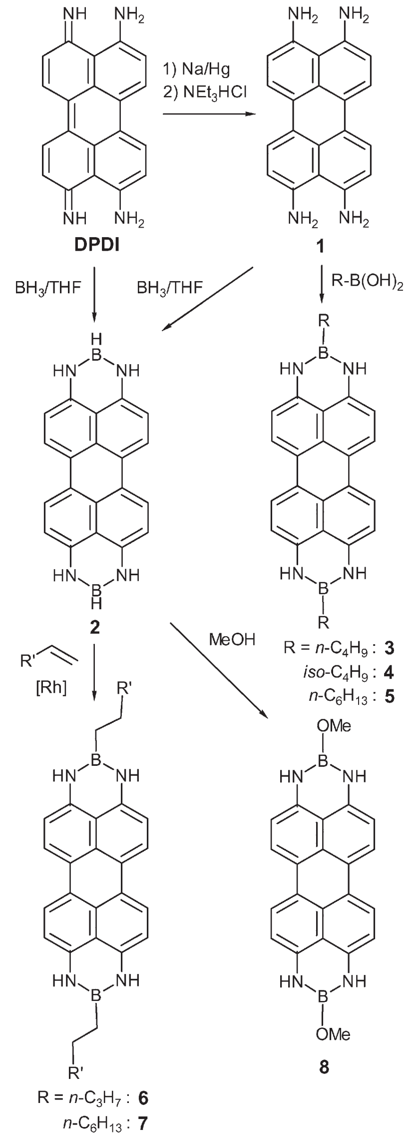
**A new class of N–B–N functionalized perylenes derived from *N*,*N*′,*N*″,*N*′′′-diborylene-3,4,9,10-tetraaminoperylene (DIBOTAP) is readily accessible *via* several synthetic routes; they display intense green fluorescence and undergo two electrochemically reversible one-electron oxidation steps at ∼ −0.2 V and 0.3 V (*vs.* SCE).**

The application of polycyclic aromatic hydrocarbons (PAH) in the development of new functional materials, in particular in the development of organic electronics, has recently led to a renaissance of their chemistry.[1] Next to polyacenes, perylene derivatives have been studied extensively, most of them derived from perylenetetracarboxdianhydride (PTCDA) or perylenetetracarboxdiimide (PTCDI).[2] Further derivatization of these species, particularly in the aromatic bay position,[3] has led to highly functional fluorescent dyes which may be used in molecular devices such as field effect transistors and organic light emitting devices.[4] Whereas most of the functional perylenes are thus derived from PTCDA, we recently developed synthetic methods which give access to the semiquinoidal 4,9-diaminoperylene-quinone-3,10-diimine (DPDI)[5] as well as 1,3,8,10-tetraazaperopyrene.[6]

A first attempt to stabilize and study derivatives of the parent compound 3,4,9,10-tetraaminoperylene (TAP) has been in the form of the tetracarboxamides.[7] As an alternative way of functionalizing the tetraaminoperylene fluorogen while retaining the planar structure of the molecular units we have now placed planar trigonal {R–B} borylene units between the two amino functions at both ends of the molecule. The N-bonded {R–B} units, located on the long molecular axis, are not expected to influence the photophysical properties of the TAP fluorogen significantly (*vide infra*), contrasting this approach with the BN units incorporated into PAHs reported by Piers and coworkers.[8] Their role will be that of points of attachment for linkers connecting TAP with other molecular fragments in the construction of more complex molecular arrays.

The synthesis of the parent *N*,*N*′,*N*″,*N*′′′-diborylene-3,4,9,10-tetraaminoperylene **2** proved to be straightforward. Nearly quantitative yields of **2** were obtained by an indirect route, by which DPDI was first reduced to 3,4,9,10-tetraaminoperylene (**1**). The latter was then reacted with two molar equivalents of the borane–THF adduct yielding the target compound **2** (Scheme 1). Alternatively, the direct reaction of DPDI with $BH_3$–THF also gave **2** in similar yield. The reduction of 1,3-diimines with



**Scheme 1** Synthesis of the diborylenetetraaminoperylenes **2–8**, exemplifying the functional versatility of this class of perylene dyes.

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[a] *Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany. E-mail: lutz.gade@uni-hd.de*
[b] *Physikalisches Institut der Universität Münster, Mendelstraße 7, 48149 Münster, Germany*

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$BH_3$–THF giving stable BH-bridged 1,3-diamines has been reported previously,[9] and we assume that the direct synthesis of **2** also occurs *via* initial hydroboration of the imino functions in DPDI and subsequent ring closure with elimination of $H_2$.

The synthesis of B-substituted derivatives of **2** may be achieved by introduction of pre-formed R–B units or by transformation of the B–H bond (Scheme 1). As an example of the former strategy, the B-alkyl derivatives **3–5** have been synthesized by reacting **1** with two molar equivalents of the corresponding alkyl boronic acids.[10] Alternatively, such species proved to be accessible by rhodium catalysed hydroboration of **2** with terminal olefins using Wilkinson's catalyst, as exemplified in the synthesis of compounds **6** and **7**.[11] Finally, the reaction of **2** with alcohols may yield the B-OR derivatives as shown in the reaction with methanol, giving the $CH_3O$-B compound **8**.

In order to established the structural details of this new class of perylene dyes, a single crystal X-ray structure analysis of compound **3** has been carried out (Fig. 1).‡ The molecules have crystallographic inversion symmetry. The polycyclic ring system is planar (rms deviation 0.009 Å), with the methylene groups of the butyl substituents only slightly displaced from the plane (max. distance 0.05(1) Å). The molecular packing is characterized by two strands of stepped π-stacks (interplanar spacing 3.44 Å), which run at an angle of 86° to each other. The carbon–carbon bond lengths within the perylene core range from 1.379(2)/1.381(2) Å [C(1)/C(3)–C(2)/C(8)] to 1.468(2) Å [C(6)–C(10)] and resemble those of the parent perylene[12] as well as the previously characterized tetrakis(pivalylamido)perylene.[7] This strongly contrasts with DPDI and tetraazaperopyrene derivatives where a more localized pattern typical of semiquinoidal aromatic systems is found.[5]

The absorption spectra of **2–8** recorded in THF are characterized by an intense band between 450 and 550 nm that has a vibrational progression of 1340–1375 $cm^{-1}$, which is typical for a $\pi^* \leftarrow \pi$ transition in perylene dyes (Fig. 2).[2–4] Molar extinction coefficients of $\log \varepsilon = 4.40$ were determined for the band maxima which are essentially unaffected by the nature of the substituents at the boron. This along with the unaltered wavelengths of the absorption maxima in **2–8** confirmed the assumption that the boron atom does not belong to the actual chromophor. This is readily appreciated on the basis of the symmetry of the system which dictates frontier orbitals having a nodal plane at the long axis of the molecules. This is shown for the Kohn–Sham HOMO (left) and LUMO (right) of the parent compound **2**.

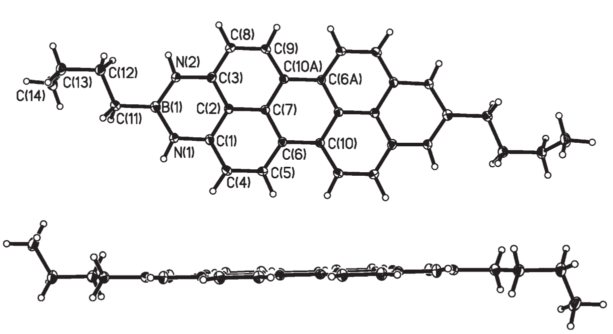


**Fig. 1** Molecular structure of **3** (top); side view of one of the stepped π-stacks (bottom). Selected bond lengths [Å] and angles [°]: B(1)–N(1)/N(2) 1.424(2)/1.415(2), B(1)–C(11) 1.564(3), C(1)/C(3)–N(1)/N(2) 1.391(2)/1.397(2), C(1)/C(3)–C(4)/C(8) 1.379(2)/1.381(2), C(2)–C(1)/C(3) 1.428(2)/1.419(2), C(2)–C(7) 1.425(2), C(4)/C(8)–C(5)/C(9) 1.396(2)/1.395(2), C(5)/C(9)–C(6)/C(10A) 1.386(2)/1.389(2), C(7)–C(6)/C(10A) 1.438(2)/1.425(2), C(6)–C(10) 1.468(2).

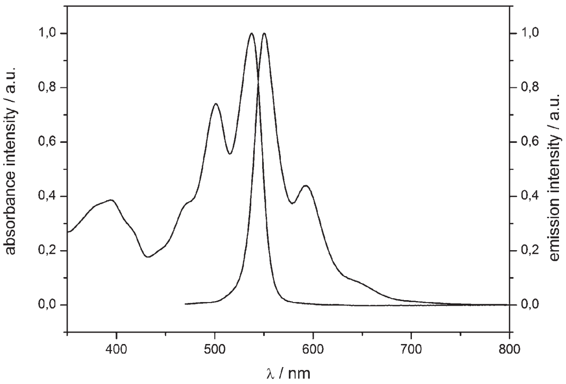
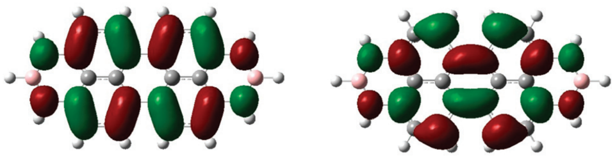


**Fig. 2** Normalized absorption and fluorescence spectra of the DIBOTAP parent compound **2** in THF.



The absorption spectrum of **2** has been computed using time-dependent-DFT methods (B3LYP/6-311g**) which gave an acceptable correspondence ($\lambda_{max}$ = 513 nm) with the experimental data (537 nm).† An improved modelling of the electronic transition accounted for the polar solvent environment (CPCM for THF) and gave a theoretical band maximum of 541 nm which is in excellent agreement with the measured spectrum. The TDDFT study also identified this transition as being almost exclusively due to the HOMO–LUMO transition, thus confirming its assignment as $\pi^* \leftarrow \pi$.

Dilute solutions of compounds **2–8** in THF display an intense green fluorescence. The emission spectrum of **2**, which is essentially identical to those of **3–8**, is also displayed in Fig. 2. The emission bands of N–B–N derivatives **2–8** display mirror symmetry with respect to their corresponding visible absorption bands and possess a pronounced vibrational progression. The observed fluorescence decay is mono-exponential for all dyes with typical lifetimes of 6 ns and quantum yields of around 65% (Table 1).

The redox-chemical properties of the highly soluble DIBOTAP derivatives **3–5** have been studied by cyclic voltammetry in THF (Table 2). Similar to tetraaminoperylene (**1**) they were readily oxidized in two consecutive one-electron steps. Oxidation occurs in two one-electron steps, at *ca.* −0.2 V (*vs.* SCE; −0.8 *vs.* $Fc/Fc^+$) to the radical cation and at approximately 0.3 V (−0.3 *vs.* $Fc/Fc^+$) to the corresponding dication (Scheme 2). At scan rates of $<50$ mV $s^{-1}$ both steps are electrochemically reversible. Compared with the perylene bisimides, which possess very similar photophysical properties, the DIBOTAP derivatives are significantly more electron rich and thus easily undergo oxidation. This may be of considerable interest for their use in *p*-channel organic field effect transistors. It also indicates a potential practical limitation, namely that of their air sensitivity.

**Table 1** Emission data of compounds **1–8** (recorded in THF): Listing of the most intense emission bands ($\lambda_{em}$/nm), the vibrational progressions ($\Delta\nu$/cm$^{-1}$), excited state lifetimes ($\tau$/ns) as well as fluorescence quantum yields ($\phi$; standard: fluorescein)

| Compound | Max. $\lambda_{em}$/nm | $\Delta\nu$/cm$^{-1}$ | Stokes shift/nm | $\tau$/ns | $\phi$ |
|---|---|---|---|---|---|
| **1** | 564 | — | 40 | 6.0 | 0.64 |
| **2** | 550 | 1318 | 13 | 5.9 | 0.65 |
| **3** | 554 | 1328 | 13 | 5.8 | 0.67 |
| **4** | 555 | 1268 | 14 | 5.6 | 0.64 |
| **5** | 554 | 1300 | 13 | 5.7 | 0.66 |
| **6** | 554 | 1300 | 13 | 5.5 | 0.65 |
| **7** | 555 | 1323 | 14 | 5.7 | 0.68 |
| **8** | 550 | 1290 | 14 | 5.6 | 0.67 |

**Table 2** Half-wave potentials of the two one-electron oxidation steps for compounds **1–5**. Cyclic voltammetry in THF; reference SCE; values in parentheses referenced against Fc/Fc$^+$ (*vs.* SCE in THF $E_0 = 0.56$ V)

| Compound | $E_1$/V | $E_2$/V |
|---|---|---|
| **1** | −0.14 (−0.70) | −0.10 (−0.66) |
| **2** | −0.23 (−0.79) | 0.32 (−0.24) |
| **3** | −0.22 (−0.78) | 0.25 (−0.31) |
| **4** | −0.24 (−0.80) | 0.29 (−0.27) |
| **5** | −0.20 (−0.76) | 0.18 (−0.38) |

These two one-electron redox processes were monitored for compound **5** (in THF) by means of spectroelectrochemistry (Fig. 3). In a first step the neutral compound (black continuous line) is converted to the radical monocation (broken line), in the second step the latter is oxidized to the semiquinoidal dication (dotted line). The formation of a dicationic semiquinoidal species, as represented in Scheme 2, is reflected in considerable spectral changes associated with this second oxidation step and the similarity of the absorption characteristics with those previously established for DPDI (Scheme 1).

In conclusion, a new class of N–B–N functionalized perylenes has proved to be readily accessible *via* several synthetic routes. In this first study we have established their photophysical properties as fluorophores. This, along with their redox chemistry, will provide the basis for their incorporation into more complex functional architectures which is currently under way in our laboratories. We thank the Fonds der Chemischen Industrie for support of this work. G.D.P. thanks the IRTG 1444 for financial support.

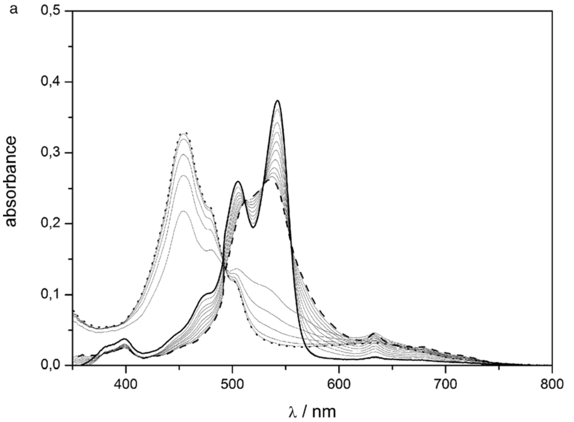
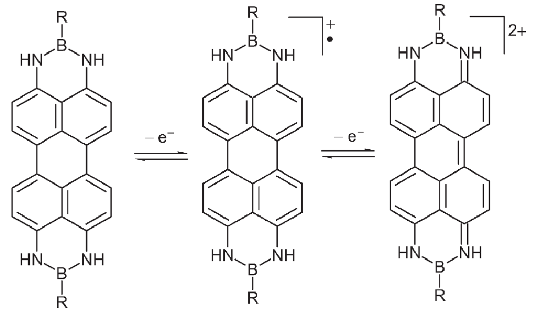


**Fig. 3** Spectroelectrochemistry of the two one electron oxidation steps for compound **5** (in THF): In a first step the neutral compound (black continuous line) is converted to the radical monocation (broken line); in the second step the latter is oxidized to the semiquinoidal dication (dotted line).



**Scheme 2** The two one-electron oxidation steps of the DIBOTAP derivatives.

## Notes and references

‡ *Crystal data:* $C_{28}H_{30}B_2N_4$, monoclinic, space group $P2_1/c$, $a$ = 9.6091(11), $b$ = 14.2555(15), $c$ = 8.2715(9) Å, $\beta$ = 104.586(2)°, $V$ = 1096.5(2) Å$^3$, $Z$ = 2, $\mu$ = 0.079 mm$^{-1}$, $F_{000}$ = 472. $T$ = 100(2) K, $\theta$ range 2.2 to 30.5°. Index ranges $h$, $k$, $l$ (indep. set): −13···13, 0···20, 0···11. Reflections measd: 26 086, indep.: 3347 [$R_{int}$ = 0.0812], obsvd [$I > 2\sigma(I)$]: 1661. Final $R$ indices [$F_o > 4\sigma(F_o)$]: $R(F)$ = 0.0618, $wR(F^2)$ = 0.1558, GooF = 0.873. Bruker AXS Smart 1000 CCD diffractometer, Mo-K$\alpha$ radiation, graphite monochromator, $\lambda$ = 0.71073 Å. Structure solution: direct methods. Refinement: full-matrix least squares methods based on $F^2$; all non-hydrogen atoms anisotropic, hydrogen atoms located and refined. CCDC 694670.

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