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Putting Group 13 Elements onto Perylenes: Highly Fluorescent N−B−N- and N−Al−N-substituted Polycyclic Aromatics

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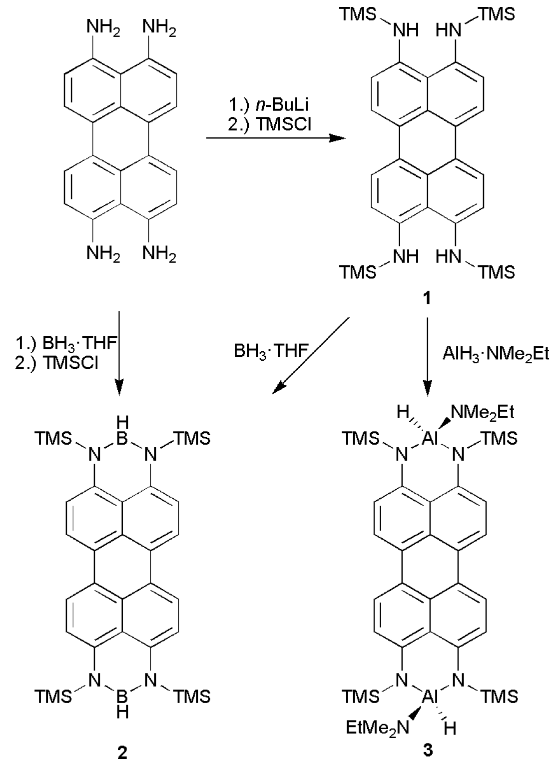
Metalation of 3,4,9,10-tetraaminoperylene with boron and aluminum complex fragments has given rise to a new class of highly fluorescent N−B−N- and N−Al−N-substituted dyes with fluorescence quantum yields of up to 82%.

Next to polyacenes, perylene derivatives have been studied extensively in the development of new functional materials, in particular in the context of organic electronics.[1] Most of these perylenes are derived from perylenetetracarboxdianhydride (PTCDA) or perylenetetracarboxdiimide (PTCDI),[2] which have given rise to highly functional fluorescent dyes that may be used in molecular devices such as field effect transistors and organic light-emitting devices.[3,4] Whereas most of the functional perylenes are thus derived from PTCDA, we recently developed synthetic methods that give access to the semiquinoidal 4,9-diaminoperylenequinone-3,10-diimine (DPDI).[5] Reduction of this semiquinoidal polycyclic aromatic compound gave access to 3,4,9,10-tetraaminoperylene (TAP), in which the amino functions may, in principle, act as *ligating units* for metals. This has now enabled us to synthesize for the first time a new class of tetra-N-substituted perylene derivatives with an aromatic core containing a further heteroatom adjacent to the two nitrogen atoms.

Scheme 1. Synthesis of Compounds **1**−**3**



The trimethylsilyl (TMS)-protected tetraaminoperylene (**1**; Scheme 1) was accessible by lithiation of tetraaminoperylene with *n*-BuLi and the subsequent addition of trimethylsilyl chloride. The compound, which had been previously generated in situ by another route and only partially characterized,[5] was isolated as a deep-red highly fluorescent material and fully characterized. The synthesis of the N−BH−N-functionalized compound **2** was achieved either by the reaction of **1** with 2 mol equiv of BH$_3$·THF (THF = tetrahydrofuran) at −60 °C or by the reaction of tetraaminoperylene with BH$_3$·THF and subsequent protection of the NH moiety with TMSCl. The corresponding N−AlH−N

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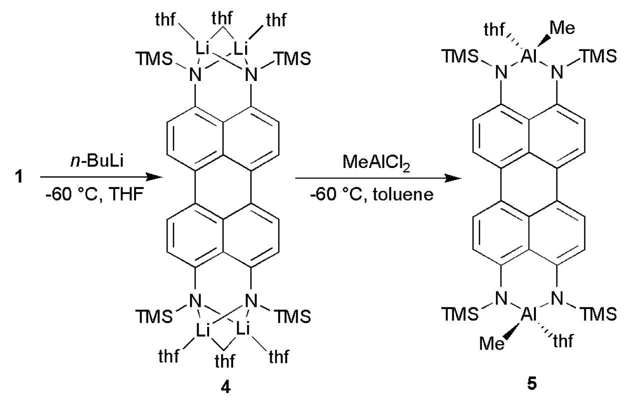
Scheme 2. Synthesis of Compounds **4** and **5**



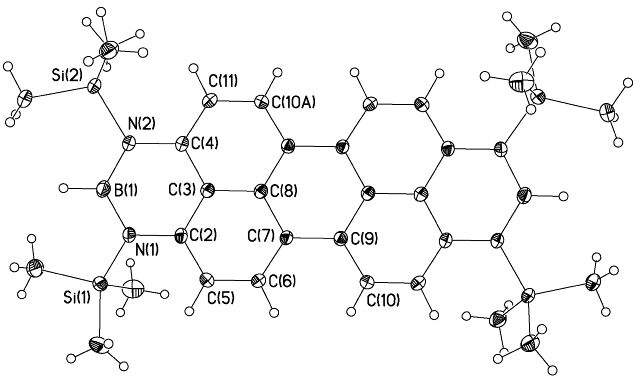


Figure 1. Molecular structure of **2**. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: N(1)−C(2) 1.417(2), N(2)−C(4) 1.418(2), N(1)−B(1) 1.426(3), N(2)−B(1) 1.424(3); C(2)−N(1)−B(1) 117.9(2), N(1)−B(1)−N(2) 122.2(2).

compound **3** was prepared by the reaction of **1** with $AlH_3 \cdot NMe_2Et$ at −60 °C.

Lithiation of **1** leads to the lithium amide **4** (Scheme 2), which could be characterized by NMR spectroscopy. The two adjacent lithium ions at the two ends of the perylenetetraamide core are solvated by three THF molecules, respectively. This form of solvation and the formulation of one THF molecule as a bridging ligand are supported by the established structures of THF adducts of diamides, which have been previously characterized by X-ray diffraction.[6] The subsequent reaction of **4** with $MeAlCl_2$ at −60 °C led to the formation of the N−AlMe−N compound **5**. For the synthesis of the aluminum compounds **3** and **5**, we followed a route applied by Roesky et al. for analogous naphthalene derivatives.[7]

Compounds **1**−**3** and **5** were characterized by multinuclear NMR and IR spectroscopy and elemental analyses. In the ^{1}H NMR of compounds **1**−**5**, the typical doublets of the chemically different perylenic core protons appear between δ 8.00−7.61 and 6.84−6.69 with a ^3J coupling constant of about 8.1 Hz. Resonances at 4.72 (**2**) and 3.73 (**3**) ppm are assigned to the BH and AlH protons, respectively.

The resonances observed in the ^{13}C NMR spectra of **1**−**5** are almost identical for the arene part. The most significant change is observed for the lithium amide **4**, where the ^{29}Si NMR signal of the TMS group is observed at δ −14.8, which is in good agreement with the corresponding naphthalene lithium amide.[5] IR bands at 2588 cm^{-1} (**2**) and 1869 cm^{-1} (**3**) are assigned to the B−H and Al−H stretching frequencies, respectively, which compare well with analogous naphthalene compounds.[7,8]

The structures of **2** and **5** were determined by single-cyrstal X-ray diffraction. The molecular structure of **2** is depicted in Figure 1 along with selected bond lengths and angles.[9] The C−N distances of 1.417 and 1.418 Å are in the range of a typical $C_{aryl}-N_{amine}$ bond (~1.42 Å in 1,8-diaminonaphthalene). The B−N bond lengths (1.42 Å) are slightly shorter than those in crystallized borazine derivatives (1.44 Å).[10] The packing pattern of compound **2** is determined by π stacking of the polycyclic aromatic ring systems. The $\pi-\pi$ plane distance is 3.6 Å, and the parallel-oriented neighboring molecules are shifted relative to each other.

The molecular structure of the aluminum derivative **5** is depicted in Figure 2.[11] The aluminum atoms adopt tetrahedral coordination with Al−N bond lengths of 1.825 and 1.827 Å. These data are again comparable to those found by Roesky et al. for the analogous naphthalene compound.[7] We note that the $\{CH_2\}_4$ unit of the coordinated THF molecule is oriented almost parallel to the aromatic perylene core.

A systematic study of the photophysics of the compounds **1**−**3** and **5** was carried out in THF. Because of the extreme sensitivity of the compounds, diluted solutions had to be handled under strict exclusion of air and moisture. The absorption spectra displayed an intense transition at around 530 nm (log ε = 4.5) with a characteristic vibrational progression of ~1300 cm^{-1} (Table 1).

As an example, the absorption and emission spectra of compound **2** in THF are depicted in Figure 3. The observation that the emission band appears as the mirror image of

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(9) Crystallographic data for **2**: $C_{32}H_{46}B_2N_4Si_4$, M = 620.71, a = 6.8710(7) Å, b = 19.769(2) Å, c = 12.6216(13) Å, b = 99.396(2)°, V = 1691.4(3) Å^3, Z = 2, space group $P2_1/c$, T = 100(2) K, λ = 0.710 73 Å, D_{calcd} = 1.219 Mg·m^{-3}, m = 0.204 mm^{-1}, $R(F)$ [$F_o > 4\sigma(F_o)$] = 0.0443, $wR(F^2)$ [all unique data] = 0.1333.

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(11) Crystallographic data for **5**: $C_{42}H_{66}Al_2N_4O_2Si_4$, M = 825.31, a = 7.1890(18) Å, b = 16.902(4) Å, c = 19.026(5) Å, b = 99.223(5)°, V = 2282(1) Å^3, Z = 2, space group $P2_1/n$, T = 100(2) K, λ = 0.710 73 Å, D_{calcd} = 1.201 Mg·m^{-3}, m = 0.207 mm^{-1}, $R(F)$ [$F_o > 4\sigma(F_o)$] = 0.0508, $wR(F^2)$ [all unique data] = 0.1341.

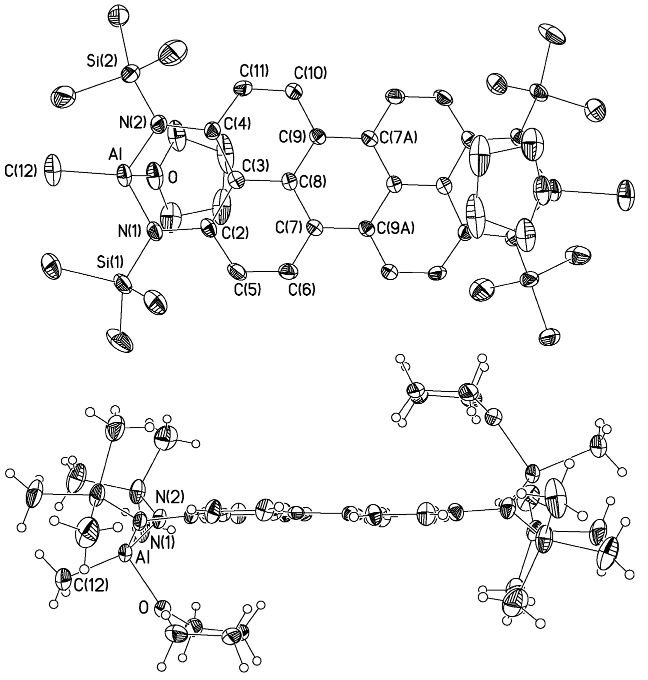

Figure 2. Molecular structure of **5** (top and side views). Displacement ellipsoids are drawn at the 50% probability level, and the hydrogen atoms in the top view are omitted for clarity. Selected bond lengths [Å] and angles [deg]: N(1)−C(2) 1.414(3), N(2)−C(4) 1.413(3), N(1)−Al 1.827(2), N(2)−Al 1.825(3), Al−C(12) 1.954(3), Al−O 1.910(2), N(2)−Al−N(1) 99.9(1), N(2)−Al−O 102.9(1), N(1)−Al−O 100.5(1), N(2)−Al−C(12) 122.6(1), N(1)−Al−C(12) 125.1(1), O−Al−C(12) 101.7(1).

Table 1. $\pi^* \leftarrow \pi$ Transitions λ_{max} [nm] and Vibrational Progression $\Delta\nu$ [cm^{-1}] in the Absorption Spectra Recorded in THF

compound	λ_{max1} (rel. int.) [nm]	λ_{max2} (rel. int.) [nm]	$\Delta\nu$ [cm^{-1}]
1	528 (0.88)	497 (0.68)	1181
2	535 (0.81)	498 (0.56)	1389
3	530 (0.89)	498 (0.69)	1212
5	531 (1.00)	497 (0.73)	1288

the lowest absorption band indicates little or no structural reorganization of the excited state and is consistent with its assignment as a $\pi^* \leftarrow \pi$ state. The Stokes shift of the emission band is only 11 nm, and the vibrational progression is 1337 cm^{-1} (Table 2).

The fluorescence lifetimes were determined between 5.2 and 7.0 ns, and the fluorescence quantum yields reach remarkably high values ranging from 50 to 82% and thus approach those determined for the well-established derivatives of perylenetetracarboxylates and -carboximides. On the basis of these data, the radiative lifetimes of the fluorophores were derived (Table 2) and found to be in good agreement with the values obtained from the stationary absorption and emission spectra by Strickler−Berg analysis (eq 1).[12]

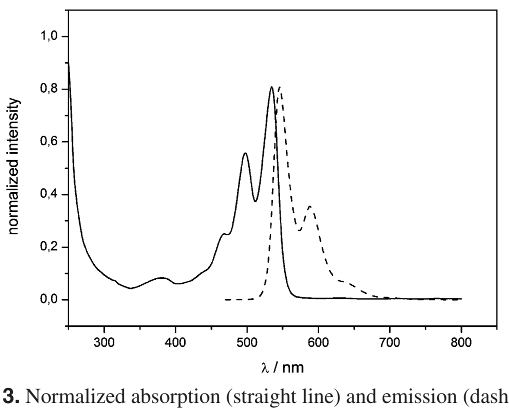

Figure 3. Normalized absorption (straight line) and emission (dashed line) spectra of **2** recorded in THF.

Table 2. Emission Data of Compounds **1**−**3** and **5** in THF

	λ_{em} [nm]	$\Delta\nu$ [cm^{-1}]	Stokes shift [nm]	τ [ns]	ϕ	τ_{rad} [ns]^a	τ_{calc} [ns]^a
1	586		58	7.0	0.82	8.5	7.8
2	546	1337	11	5.2	0.80	6.5	8.7
3	586		56	5.2	0.50	10.4	7.9
5	586		55	5.8	0.77	7.5	9.8

[a] $\tau_{rad} = \tau/\phi$ (radiative lifetime); τ_{calc} = radiative lifetime calculated with the Strickler−Berg equation. The vibrational progression was only resolved in the fluorescence spectrum of **2**.

$$\frac{1}{\tau_0} = 2880\times10^{9}\eta^{2}\frac{\int I(\nu)\,\mathrm{d}\nu}{\int \nu^{-3}I(\nu)\,\mathrm{d}\nu}\int\frac{g(\nu)}{\nu}\,\mathrm{d}\nu \qquad (1)$$

The tetraaminoperylene derivatives reported in this work illustrate the possibility of employing them as ligands for metals (or metalloids) with small ionic radii. In view of the established coordination chemistry of 1,8-diaminonaphthalene derivatives as ancillary ligands for main-group and transition metals,[13] a broad spectrum of such derivatizations appears possible. This will allow a systematic study into the way such coordination modifies the photophysics of the polycyclic aromatic fluorophore.

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Supporting Information Available: Details of the preparation and characterizing data of compounds **1**−**5**, description of the photophysical measurements, and X-ray crystallographic file in CIF format for the structure determination of **2** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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