Substituted Diazadibenzoperylenes: New Functional Building Blocks for Supramolecular Chemistry**

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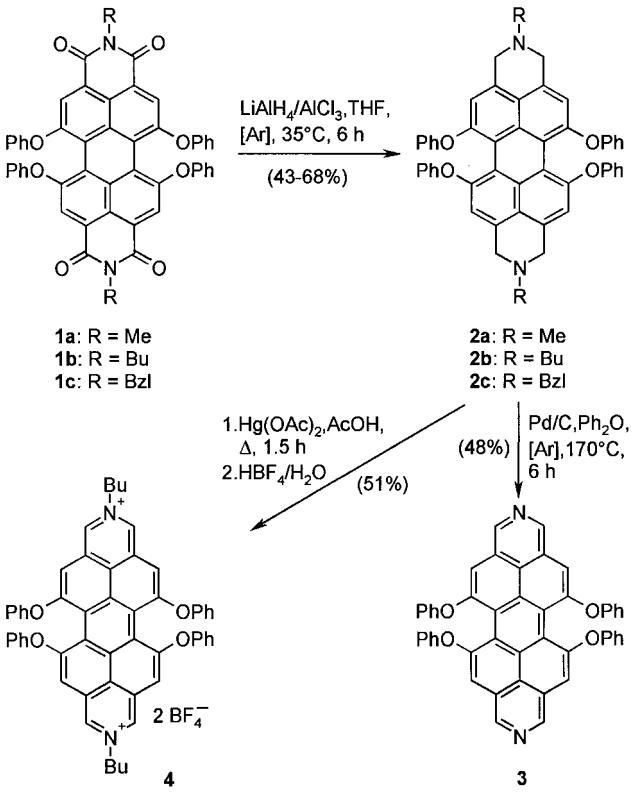
Dedicated to Professor Franz Effenberger on the occasion of his 70th birthday

Supramolecular structures are often compared to non-covalently assembled functional units in nature. To introduce functionality in artificial superstructures, building blocks are required that exhibit suitably positioned receptor groups, good solubility, as well as optical or electrical properties. Among the most widely used receptor groups in supramolecular chemistry are azaaromatic Lewis bases that can form strong intermolecular interactions with carboxylic acids, Lewis acidic boron compounds, and metal centers.[1] In particular ditopic building blocks such as pyrazine, 4,4′-bipyridine, and diazapyrene have been used to construct sandwich complexes with coordinated metalloporphyrins, molecular squares with ligand-bridged Pd and Pt corners, cage compounds, polymeric aggregates, and solid-state networks.[2] Herein we describe the synthesis of a new "expanded" building block, 5,6,12,13-tetraphenoxy-2,9-diazadibenzo[*cd*,*lm*]perylene (**3**), and its functional and coordinative properties.

Our synthesis starts with phenoxy-substituted perylene bisimides **1a–c**,[3, 4] which could be reduced to the amines **2a–c** with lithium aluminum hydride/$AlCl_3$.[5a] The subsequent aromatization reaction turned out to be critical, because amines **2a–c** decompose under the drastic reaction conditions which are typically used to accomplish dehydrogenation and dealkylation.[5a–c] Finally **3** could be obtained under comparably mild reaction conditions from **2c** because the benzyl (Bzl) groups were readily removed in the presence of Pd/C (Scheme 1).

Diazadibenzoperylene **3** is isolated as a bright red, poorly crystallizing solid and shows an intense yellow-green fluorescence in solution and a red solid-state fluorescence. The compound exhibits excellent solubility in halogenated hydrocarbons and is even soluble in aliphatic solvents (>300 gL^{-1} in CH_2Cl_2; 0.6 gL^{-1} in cyclohexane).

Oxidation of dibutyl-substituted perylene **2b** with mercury(II) acetate[5a] affords the dibutyldiazadibenzoperylenium dication which crystallizes readily as tetrafluoroborate salt **4**



Scheme 1. Synthesis of substituted diazadibenzoperylenes **3** and **4**.

(Scheme 1). Single crystals suitable for X-ray crystal structure analysis were obtained by layering a solution of **4** in dichloromethane/methanol with diethyl ether (Figure 1). As expected all C–C bond lengths of the diazadibenzoperylene backbone

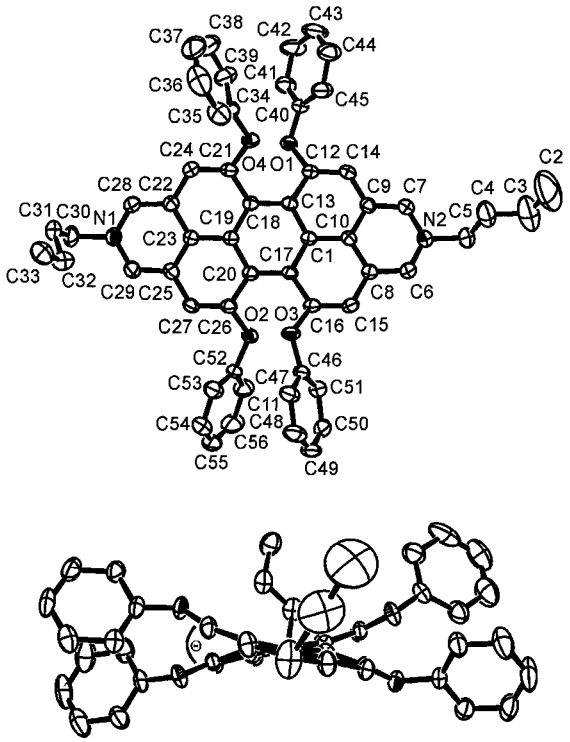


Figure 1. Structure of **4** in the crystal (ORTEP plot). The hydrogen atoms and BF_4 counterions were omitted for clarity (top). View along the N–N axis showing the twisted perylene backbone ($\Theta = 25°$) (bottom).

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are between 1.35 and 1.45 Å, which confirms a high degree of conjugation. Owing to the electrostatic repulsion between the oxygen atoms of the phenoxy substituents, the central six-membered ring is twisted by 25° (Figure 1). This twisting, which interferes with $\pi-\pi$ stacking of the extended aromatic surfaces, is considered to be important for the excellent solubility properties of **3** and **4**.

The absorption spectra are characterized by intense absorption bands with maxima at 496 nm (**3**) and 501 nm (**4**). The emission spectra show Stokes shifts of 26 nm (**3**) and 30 nm (**4**) (Figure 2), and the fluorescence quantum yields are

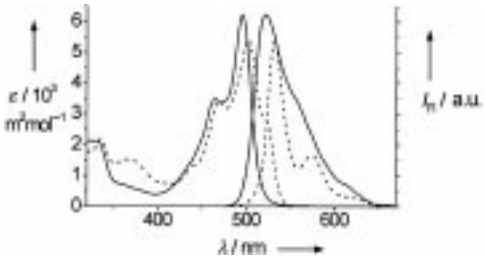


Figure 2. UV/Vis absorption and fluorescence spectra of **3** (——) and **4** (- - - -) in dichloromethane.

0.75 for **3** and 0.50 for **4** in chloroform.[6, 7] The cyclic voltammogram[8] of diaza ligand **3** (Figure 3) shows one reversible wave in the reductive cycle where reduction to the

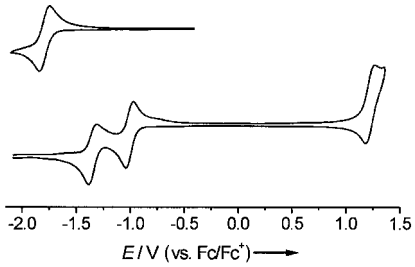
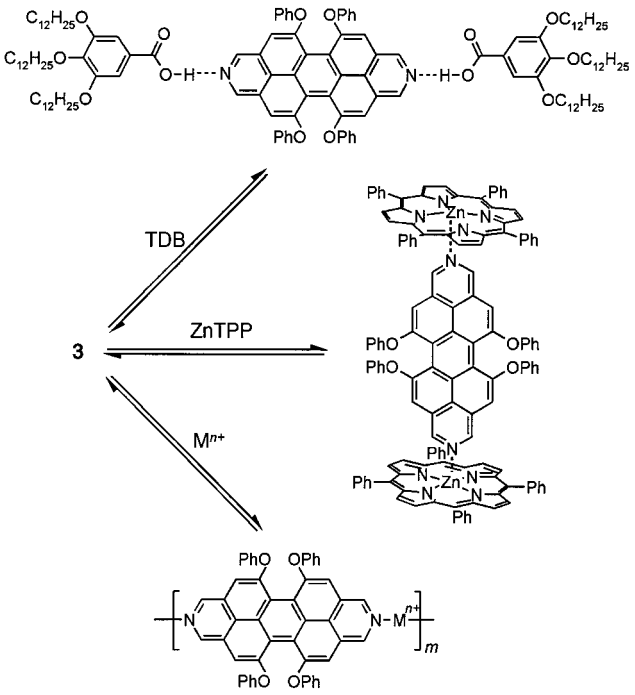


Figure 3. Cyclic voltammogram of **3** (top) and **4** (bottom) in dichloromethane (sweep rate 100 mV s^{-1}).

radical anions $\mathbf{3}^{\bullet-}$ takes place (−1.79 V versus ferrocene/ferrocenium (Fc/Fc^+)). Oxidation is irreversible and accompanied by adsorption of **3** on the electrode surface. After several oxidation cycles a stable film is deposited on the platinum electrode which itself exhibits electrochemical activity. For the alkylated ligand **4** which bears two positive charges, two reversible waves are observed in the reductive cycle, reducing **4** via the radical cation to the neutral compound (−1.01 V, −1.35 V versus Fc/Fc^+). In the oxidative cycle, a reversible oxidation to the radical trication becomes possible (+1.23 V versus Fc/Fc^+), because **4**, in contrast to **3**, does not contain lone pairs of electrons at the nitrogen atom.

The suitability of the new diaza ligand **3** as a photo- and redox-active supramolecular building block was investigated by complexation experiments with carboxylic acids (3,4,5-trisdodecyloxy benzoic acid, TDB), zinc tetraphenylporphyrin (ZnTPP), Pd^{2+} metal ions (*trans*-$[Pd(PPh_3)_2(OTf)_2]$)(Tf = F_3CSO_2) and Ag^+ ions (AgOTf) (Scheme 2). When available,



Scheme 2. Assembly of supramolecular structures by different intermolecular interactions.

highly soluble monotopic binding partners were used and the binding constants were determined by means of titration experiments monitored by NMR and UV/Vis spectroscopy.

For the hydrogen-bonding interaction of **3** with the carboxylic acid TDB we determined a binding constant of 140 M^{-1} in deuterated chloroform. The interaction between **3** and ZnTPP is considerably stronger revealing binding constants of 1500 M^{-1} in chloroform and 3900 M^{-1} in the less polar solvent CCl_4 according to UV/Vis and NMR titrations (Figure 4).[9] The binding constants for the interaction be-

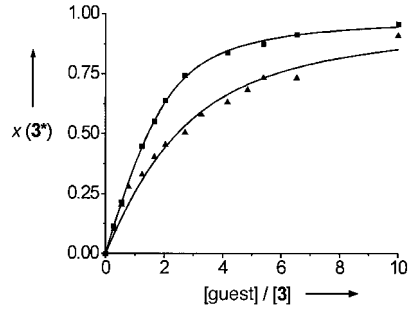


Figure 4. Amount (%) of complexed aza receptors (**3***) during titration experiments with ZnTPP (■) and TDB (▲) in $CDCl_3$. The chemical shifts of the CH protons in α-position to the nitrogen atom were monitored; they changed from $\delta = 9.22$ to 9.28 (TDB) and 3.53 (ZnTPP), respectively.

tween **3** and *trans*-$[Pd(PPh_3)_2(OTf)_2]$ as well as AgOTf ($CDCl_3/CD_3NO_2$) are too high to be determined by NMR titration experiments. During the NMR titration of **3** with Ag^+ ions a distinct signal broadening and an increase of the solvent viscosity in the NMR tube is noted when a 1:1 stoichiometry is approached. Both observations indicate the formation of a coordination polymer.

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Experimental Section

2c: $AlCl_3$ (7.48 g, 56 mmol) and $LiAlH_4$ (2.13 g, 56 mmol) were added to cooled (ice bath) dry THF (300 mL) under argon. After removal of the cooling bath, perylene bisimide **1c** (6.56 g, 7 mmol) was added in small portions. The mixture was stirred at 35 °C for 6 h and then poured into 1.4 L of cold 0.3 N hydrochloric acid and stirred for 1 h. The precipitate was suction filtered, washed with H_2O and dried. It was suspended in methanol (200 mL) and 1N NaOH (50 mL) was added to precipitate the yellow amine **2c** which was collected, washed neutral, dried, and purified by chromatography on a Merck Lobar C column (4.20 g, 68 %): m. p. 252 °C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.34 - 7.21$ (m, 10H), 7.16 (t, $J = 8.0$ Hz, 8H), 6.97 (tt, $J = 7.4$, 1.1 Hz, 4H), 6.82 (md, $J = 8.6$ Hz, 8H), 6.80 (s, 4H), 3.82 (s, 8H), 3.71 (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): $\delta =$ 157.0, 152.9, 137.7, 135.0, 133.1, 129.24, 129.19, 128.4, 127.3, 122.6, 120.5, 119.4, 115.7, 114.5, 61.9, 56.0; UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon) = 453$ (26200), 429 (22100), 381 (5200), 360 (3700), 298 (57000), 259 (31000) nm; field desorption (FD) MS (8 kV): *m/z* (%): 882 ($[M]^+$, 100); elemental analysis (%): calcd for $C_{62}H_{46}N_2O_4$ (883.06): C 84.33, H 5.25, N 3.17; found: C 84.33, H 5.26, N 3.07.

2b: As described for **2c** but the reaction was carried out under reflux for 3 h. 50 %: m. p. 208 – 210 °C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.16$ (m, 8H), 6.96 (m, 4H), 6.84 – 6.82 (m, 12H), 3.79 (s, 8H), 2.52 (t, $J = 7.4$ Hz, 4H), 1.55 (m, 4H), 1.32 (m, 4H), 0.89 (t, $J = 7.3$ Hz); UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon) = 454$ (24800), 430 (20600), 362 (3700), 300 (55500), 258 (30600) nm; elemental analysis (%): calcd for $C_{56}H_{50}N_2O_4$ (815.03): C 82.53, H 6.18, N 3.44; found: C 82.40, H 6.30, N 3.40.

3: A mixture of **2c** (2.65 g, 3 mmol) and 0.32 g Pd/C (10 % Pd) was stirred under argon in diphenyl ether (150 mL) for 6 h at 170 °C. After cooling, the mixture was filtered over celite/silica gel (each ca. 5 cm), and diphenyl ether was eluted with CH_2Cl_2. The product was eluted with an increasing amount of methanol, and the solvent was evaporated. After chromatography on a Merck Lobar C column (CH_2Cl_2/MeOH 97:3) **3** was isolated as a bright red solid (1.00 g, 48 %): m. p. 273 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 9.21$ (s, 4H), 7.52 (s, 4H), 7.34 (t, $J = 7.6$ Hz, 8H), 7.18 (tt, $J = 7.5$, 1.1 Hz, 4H), 7.13 (md, $J = 7.6$ Hz, 8H); ^{13}C NMR (126 MHz, $CDCl_3$, 20 °C): $\delta = 156.6$, 155.8, 143.3, 129.9, 126.8, 125.8, 124.4, 120.8, 120.2, 108.14, 108.13; UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon) = 496$ (62300), 465 (34900), 307 (22500), 294 (21800), 270 (47000) nm; EI-MS: *m/z* (%): 696 ($[M]^+$, 100); elemental analysis (%): calcd for $C_{48}H_{28}N_2O_4$ (696.76): C 82.74, H 4.05, N 4.02; found: C 82.41, H 3.95, N 4.09.

4: A mixture of **2b** (0.41 g, 0.5 mmol) and $Hg(OAc)_2$ (0.64 g, 2.0 mmol) in acetic acid (20 mL) was stirred under reflux for 1.5 h. The mixture was cooled to room temperature, filtered, and H_2O (15 mL) and HBF_4 (1 mL; 50 % aqueous solution) were added to yield a brown precipitate which was separated and washed with a small amount of H_2O/MeOH (1:1). After drying, the crude product was purified by column chromatography on silica gel (CH_2Cl_2/MeOH 9:1) and recrystallized from methanol/diethyl ether. Compound **4** was isolated as an orange crystalline solid (0.25 g, 51 %): m. p. 272 – 275 °C (decomp); ^{1}H NMR (500 MHz, [D$_6$]acetone, 20 °C, $\delta = 2.04$): $\delta = 9.92$ (s, 4H), 8.03 (s, 4H), 7.50 (t, $J = 7.9$ Hz, 8H), 7.35 (t, $J = 7.5$ Hz, 4H), 7.30 (d, $J = 7.8$ Hz, 8H), 5.18 (t, $J = 7.2$ Hz, 4H), 2.29 (m, 4H), 1.50 (m, 4H), 0.96 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (126 MHz, [D$_6$]acetone, 20 °C): $\delta = 160.0$, 155.5, 137.5, 131.3, 130.0, 127.1, 126.7, 123.1, 121.87, 121.83, 108.7, 63.7, 34.4, 20.0, 13.7; UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon) = 502$ (55000), 469 (35200), 367 (15500), 335 (22300), 301 (64700), 260 (51800) nm; elemental analysis (%): calcd for $C_{56}H_{46}N_2O_4B_2F_8$ (984.60): C 68.31, H 4.71, N 2.85; found: C 68.23, H 4.71, N 2.81.

Crystal structure analysis of **4**: $C_{56}H_{46}B_2F_8N_2O_4$, $M_r = 984.60$, monoclinic, space group $P2_1/n$ (no. 14), $a = 12.8868(16)$, $b = 21.825(5)$, $c = 17.688(2)$ Å, $\beta = 99.743(14)°$, $V = 4903.2(14)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.334$ Mg m^{-3}, $\mu(Mo_{K\alpha}) =$ 0.103 mm^{-1}, crystal size $0.19 \times 0.31 \times 0.62$ mm, $T = 220$ K, 9285 independent reflections collected, 682 parameters, $R1 = 0.0565$ and $wR2 = 0.1366$ for reflections with $I > 2\sigma(I)$, max./min. residual electron density 0.419/ -0.306 e Å^{-3}. Data were collected using a STOE-IPDS-diffractometer with monochromatic (graphite monochromator) $Mo_{K\alpha}$ radiation ($\lambda =$ 0.71073 Å, $2\theta_{max} = 51.94°$, $2\theta_{min} = 4.08°$); scan modus rotation. The structure was solved by direct methods (SHELXS 97),[10a] (refinement on F^2 using the full-matrix least-squares method (SHELXL 97).[10b] Hydrogen atoms were set geometrically as idealized CH_2, CH_3, and aromatic CH groups and treated using a riding model. The tetrafluoroborate anions showed a strong orientation disorder and were described and refined by using 10 and 12 fluorine split sets, respectively, but the exact positions of the fluorine atoms could not be determined.[11] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133189. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[6] Optically dilute method with refractive index correction, maximum absorptions of the solution ≤ 0.035. Calibrated spectrometer; all fluorescence spectra were corrected. Measurements relative to fluorescein in 0.1N NaOH ($\Phi_{ref} = 0.9$).[7b]

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[8] Cyclic voltammetry was measured in dichloromethane (distilled from H_2SO_4 and filtered over basic aluminum oxide). Working electrode: platinum disk; counter electrode: platinum wire; Ag/AgCl reference electrode; supporting electrolyte: tetra-*n*-butylammonium hexafluorophosphate (0.1M); internal standard: ferrocene. The approximately 10^{-3}M solutions were purged with argon.

[9] All titration experiments were evaluated by assuming two independent receptor sites for host **3** and a negligible self-association of the guest molecules (TDB, ZnTPP) within the investigated concentration range.

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