Synthesis of Diazadibenzoperylenes and Characterization of Their Structural, Optical, Redox, and Coordination Properties

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Tetraphenoxy-substituted diazadibenzoperylenes **5a**,**b** were synthesized from tetrachloroperylene tetracarboxylic acid bisanhydride **1** through imidization with benzylamine, nucleophilic displacement of the four chlorine atoms by phenolates, carbonyl group reduction by $LiAlH_4/AlCl_3$, and subsequent Pd/C-promoted debenzylation−dehydrogenation. The structural properties of these extended diazaarenes are discussed on the basis of a X-ray crystal structure of the N,N'-dibutylated diazadibenzoperylenium dication **6**, which revealed a 25° twist of the central six-membered ring leading to an atropisomeric π-conjugated backbone. The chromophoric systems of **5** and **6** were characterized by optical absorption and fluorescence spectroscopy, which revealed an intense fluorescence with a quantum yield of 75% for **5** and 50% for **6**. Cyclic voltammetry showed reversible oxidation and reduction waves for **6**, whereas the oxidation of **5** afforded the irreversible deposition of a conductive film on the electrode surface. Finally, the potential use of ligands **5** in supramolecular chemistry has been evaluated by complexation experiments with carboxylic acids and zinc tetraphenylporphyrin (ZnTPP).

Introduction

Supramolecular architectures of π-conjugated molecules are often compared to the noncovalently assembled dye aggregates found in the light-harvesting complexes of photosynthetic plants and bacteria.[1,2] Inspired by the intriguing functionality of the natural assemblies, most of the artificial mimicries presently available are based on bio-inspired chromophores such as porphyrins, chlorines, and carotenes.[1] However, to realize different kinds of functionality in supramolecular assemblies that might open attractive applications in fields such as (supra-)molecular electronics, solar cells, or field effect transistors, a higher structural and functional diversity of the available dyes is desirable. To be useful for such goals, the respective dyes should contain suitably positioned receptor groups for directional intermolecular interactions, high solubility, as well as favorable optical and/or electrochemical 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.[3] In particular, ditopic building blocks such as pyrazine, 4,4′-bipyridine, and diazapyrene have been used to construct sandwich complexes with coordinated metalloporphyrins, catenanes and rotaxanes, molecular squares with ligand-bridged Pd(II) and Pt(II) corners, cage compounds, polymeric aggregates, or solid-state networks.[4] Recently, we introduced an extended and functionally enriched version of these π-systems, i.e., diazadibenzoperylene **5a**,[5] which proved to exhibit exciting supramolecular properties including the formation of triangular and square metallacycles upon coordination to *cis*-Pt(II) and *cis*-Pd(II) metal corners[6] as well as the formation of columnar liquid crystals after covalent or hydrogen-bonded attachment of mesogenic substituents.[7] In this paper, we give details about the synthesis of these interesting supramolecular building blocks and describe their structural, optical, and electrochemical properties as well as the strength of their noncovalent interaction

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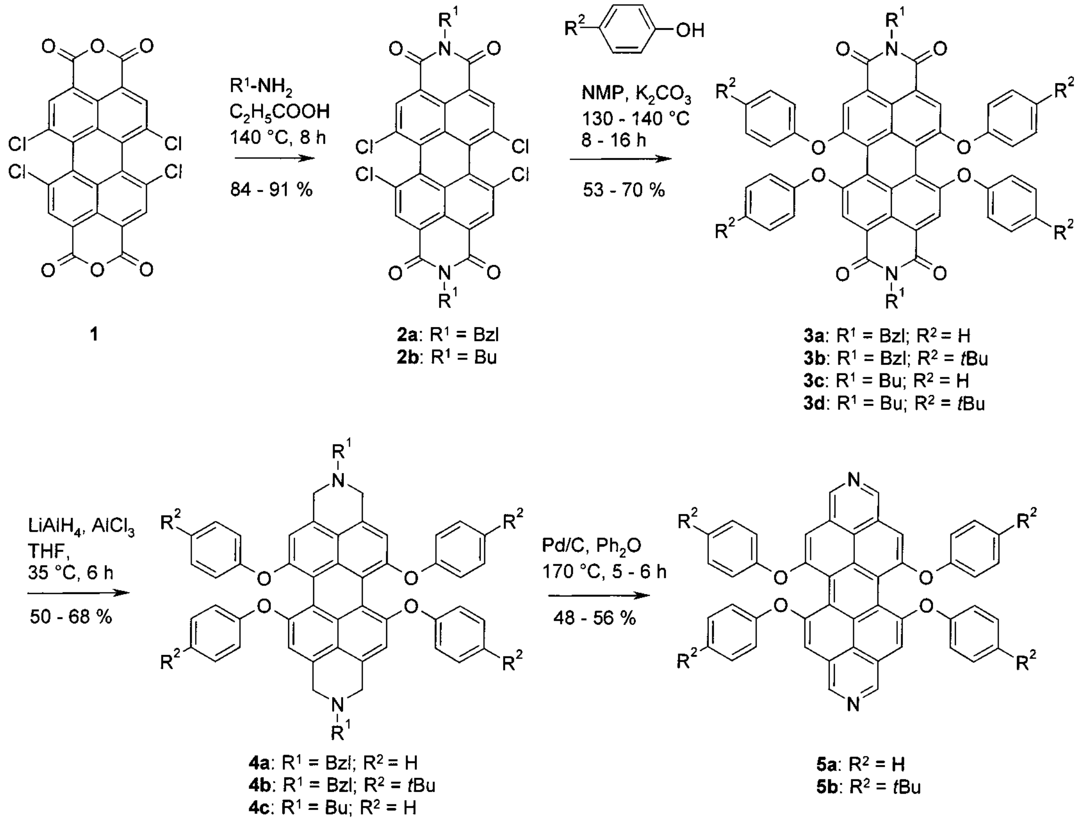
Scheme 1



to carboxylic acids and zinc metal ions of zinc tetraphenylporphyrins (ZnTPP).

Results and Discussion

Synthesis. The synthesis of core-substituted diazadibenzoperylenes **5a**,**b** follows the strategy outlined in Scheme 1, which was inspired by the synthesis of 2,7-diazapyrene described by Hünig et al.[8] and of 2,9-diazadibenzoperylene by Stang et al.[9a] Tetrachloroperylene bisanhydride **1** was reacted with butyl- and benzylamine in propionic acid to give the tetrachloroperylene bisimides **2a**,**b**. In this reaction, not only the nitrogen atoms are introduced but also two alkyl groups that have to be removed in the last step. It was found that the use of benzyl substituents is preferable over butyl, as benzyl groups sufficiently solubilize the perylenes **2**−**4** and can be cleaved under rather mild conditions (vide infra). The subsequent displacement of the chlorines by phenolate and 4-*tert*-butylphenolate yielded tetraphenoxyperylene bisimides **3a**−**d**,[2,10] which could be reduced by lithiumaluminum hydride/aluminum chloride to give the amines **4a**−**c**. However, the final step, which requires both cleavage of alkyl groups and aromatization by dehydrogenation, imposed difficulties. Application of standard reaction conditions described in the literature[8,9] were not successful.[5b] For example, typical dehydrogenations by Pd/C are conducted in the molten state of the compounds at about 300 °C, conditions that are not applicable to the thermally rather sensitive amines **4a**−**c**. For **4a**,**b**, decomposition is already complete when the compounds are molten (TLC check), and even storage at ambient conditions (room temperature, air) leads to slow decomposition that manifests in a color change from bright yellow to dark brown. For this reason, the aromatization reaction with Pd/C had to be optimized, which was possible for the benzylated compounds **4a**,**b** by lowering the reaction temperature and conducting the reaction in an appropriate solvent[9c] (Table 1).

Table 1. Optimization of the Debenzylation−Dehydrogenation Reaction of 4a with Pd/C[a]

solvent	*T* (°C)	*t* (h)	isolated yield (%)
naphthalene	218	2	30
cumene	152	4	28
diphenyl ether	170	6	48
toluene	111	9	–

[a] The reactions were terminated when no more **4a** was detected by thin-layer chromatography.

According to Table 1, the reaction of **4a** in boiling naphthalene at 218 °C afforded a considerably improved yield. Similar results were obtained at 152 °C in refluxing cumene, but still decomposition was predominant. When the temperature was further decreased to 111 °C in boiling toluene, no conversion took place anymore. Finally, upon changing to diphenyl ether as solvent, less decomposition and side reactions were noted leading to the best yields at a temperature of 170 °C (6 h, 48%). Below 170 °C, the reaction was found to be rather slow, and above this temperature decomposition rapidly increased. These conditions (diphenyl ether, 170 °C, 6 h) could be successfully applied for the synthesis of diaza-

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(8) Hünig, S.; Groβ J.; Lier, E. F.; Quast, H. *Liebigs Ann. Chem.* **1973**, 339.

(9) (a) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6272. (b) Fu, P. P.; Harvey, R. G. *Chem. Rev.* **1978**, *78*, 317. (c) Chen, Q.; Deady, L. W. *Aust. J. Chem.* **1993**, *46*, 987.

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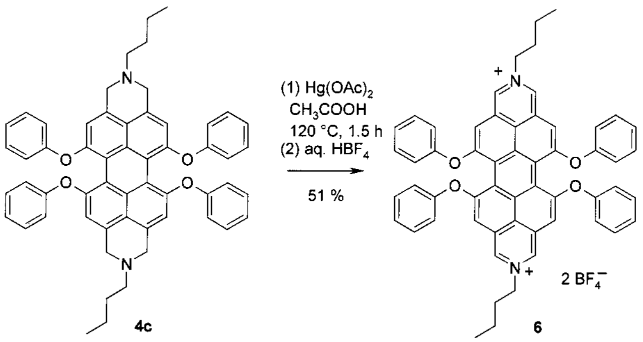
dibenzoperylene **5b** in 56% isolated yield. Despite the extended aromatic surfaces and the lack of solubilizing alkyl chains in **5a**,**b**, these compounds exhibit a remarkable solubility. For example, the solubility of **5a** in dichloromethane exceeds 300 g L^{-1} and is still 0.6 g L^{-1} in cylohexane.

Structural Properties. An unsuccessful effort in the synthesis of diazadibenzoperylene **5a** involved the *N*,*N*′-dibutylated derivative **4c**, but failed in the removal of the butyl groups in the final high-temperature aromatization step.[5b] However, oxidation of the *N*,*N*′-dibutyl-substituted perylene diamine **4c** with mercury(II) acetate[8] gave the *N*,*N*′-dibutyldiazadibenzoperylenium dication whose precipitation with tetrafluoroborate anions afforded well-defined crystals of **6**.



This is remarkable as core-substituted perylene derivatives do not crystallize well,[2,10] and only one crystal structure of a phenoxy-substituted perylene derivative has been reported so far.[11] On the other hand, many crystal structures are known for unsubstituted perylene bisimide pigments that have been thoroughly studied by Graser and Hädicke.[12]

Single crystals suitable for X-ray crystal structure analysis were obtained by layering a solution of **6** in dichloromethane/methanol with diethyl ether. An ORTEP plot of **6** is depicted in Figure 1. As expected, all C−C bond lengths of the diazadibenzoperylene backbone are between 1.35 and 1.45 Å, which confirms a high degree of conjugation and aromaticity (Figure 1A).[13] Owing to the electrostatic repulsion between the oxygen atoms of the phenoxy substituents, the central six-membered ring gets twisted by 25° (Figure 1B) leading to an axial chirality with *P* and *M* enantiomers of **6**. The crystal of **6** is racemic, and both enantiomers are found in a 1:1 ratio in the crystallographic unit cell (only the *M* enantiomer is displayed in Figure 1). Axial chirality of tetraphenoxy-substituted perylenes is a conformational isomerism, and the energy barrier for the interconversion between the two enantiomers in solution is supposed to be very low. As a consequence, earlier attempts to isolate these highly interesting chiral dyes failed,[14] and their structural features could now be characterized for the first time in the crystalline state. In addition to the interesting implications of this twisting with regard to future work directed toward chiral dyes, this prominent twisting of the aromatic backbone is also considered to be of major importance for the excellent solubility of dyes **5** and **6** because it interferes with the stacking of the π-conjugated systems.

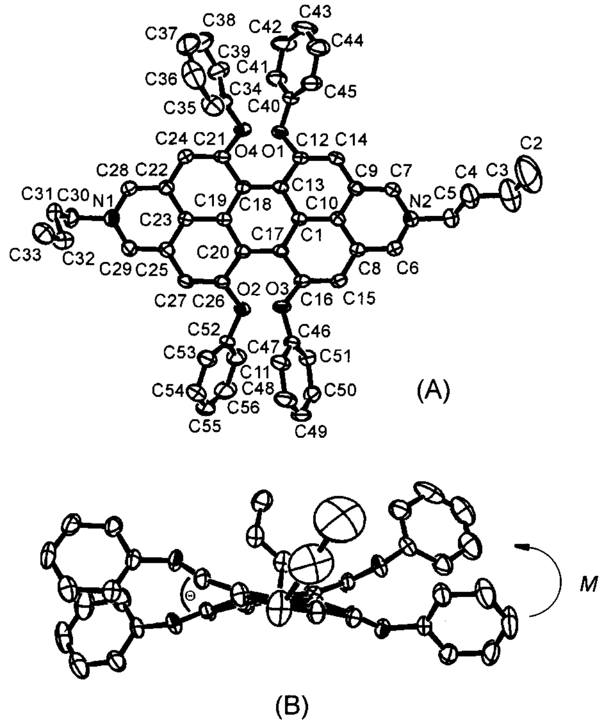


Figure 1. Structure of **6** (*M* enantiomer) in the crystal (ORTEP plot). The hydrogen atoms and BF_4^- counterions were omitted for clarity. (A) Top view and (B) view along the N−N axis showing the twisted diazadibenzoperylene backbone ($\Theta = 25°$).

The crystals belong to the monoclinic space group $P2_1/n$ with four molecules in the unit cell ($Z = 4$), i.e., two *P* and two *M* enantiomers of **6**. The arrangement of the molecules can be best visualized in a stereoview along the *c*-axis (Figure 2A,B), revealing a herringbone motif of tilted stacks of molecules that form layers. The diazadibenzoperylene backbones are oriented perpendicular with respect to the layer planes. The arrangement of the molecules within a layer and with respect to the next layer is sketched in a simplified way in Figure 2C. All molecules within a layer are of the same enantiomer, i.e., the dark molecules (top layer) are the *M* enantiomers and the light molecules (bottom layer) are the *P* enantiomers. Centers of symmetry (points of inversion) are located between the layers and bring the *P* enantiomers into coincidence with the *M* enantiomers, and vice versa (3 ↔ 4 in Figure 2C). Furthermore, there are screw axes in the direction perpendicular to the stacks. A rotation around this axis by 180° followed by a translation brings the like enantiomers into superposition (1 ↔ 2 in Figure 2C).

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[11] (a) Quante, H. Ph.D. Thesis, Universität Mainz, Germany, 1995. (b) A X-ray crystal structure of an 8-fold chlorinated perylene bisimide has also been reported: Sadrai, M.; Bird, G. R.; Potenza, J. A.; Schugar, H. J. *Acta Crystallogr. C* **1990**, *46*, 637.

[12] (a) Graser, F.; Hädicke, E. *Liebigs Ann. Chem*. **1980**, 1994. (b) Graser, F.; Hädicke, E. *Liebigs Ann. Chem*. **1984**, 483. (c) Klebe, G.; Graser, F.; Hädicke, E.; Berndt, J. *Acta Crystallogr. B* **1989**, *45*, 69.

[13] The ^{1}H NMR resonance for the protons α to the nitrogens changes from $\delta = 3.79$ (**4c**) to 9.21 (**5a**) and 9.92 ppm (**6**) supporting a high degree of conjugation and aromaticity within the diazadibenzoperylene backbone. The perylene core protons appear at $\delta = 8.03$ ppm for **6** and at 7.52 ppm for **5a**.

[14] (a) Hien, S. Diploma Thesis, Universität Regensburg, Germany, 1992. (b) Hien, S. Ph.D. Thesis, Universität Regensburg, Germany, 1995.

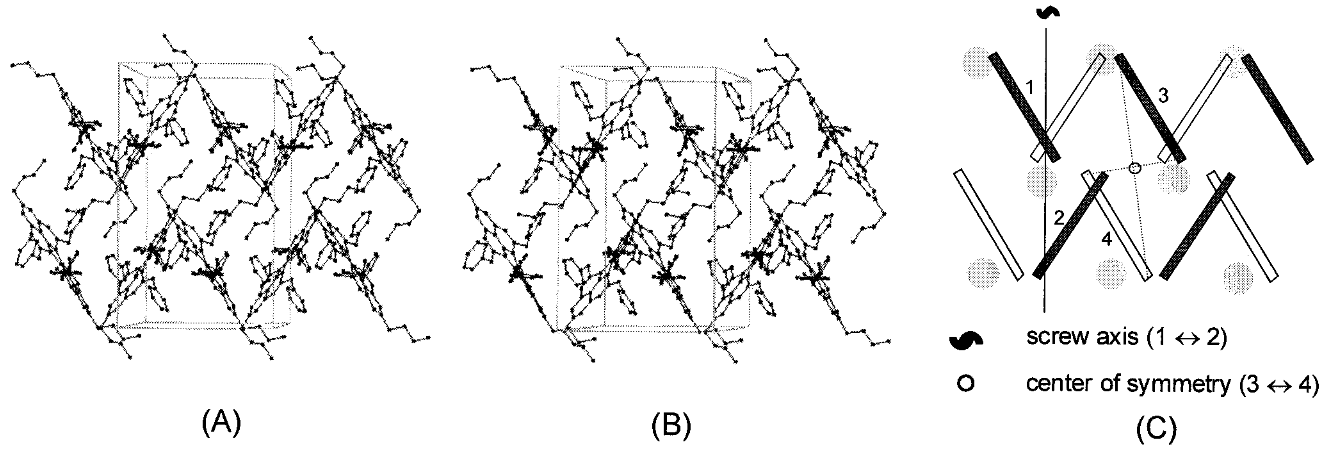


Figure 2. (A, B) Stereoview of the molecular packing in the crystal along the *c*-axis. (C) Simplified sketch of the molecular packing: the dark (*M* enantiomers) and the light (*P* enantiomers) rectangles each represent molecules within a layer (herringbone motif). The anions are located between the layers and are depicted as gray circles. One screw axis (within the layer) and one center of symmetry (between the layers) are depicted.

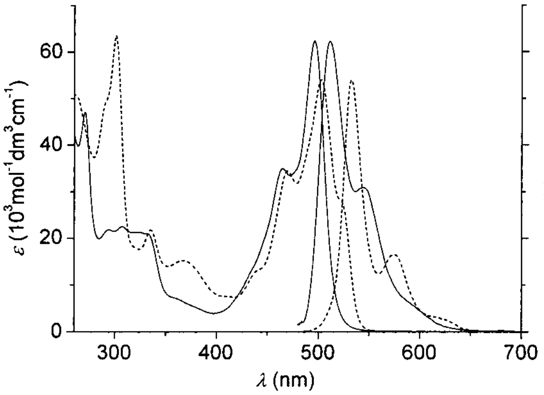


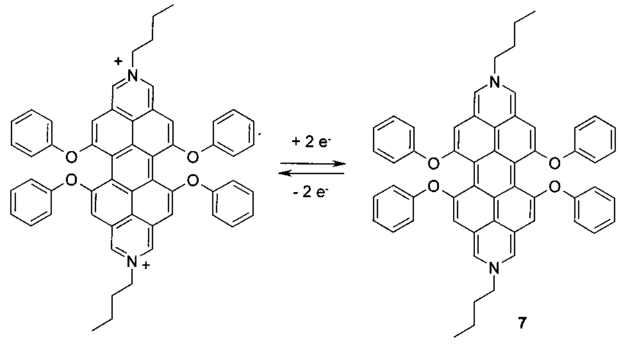
Figure 3. UV/vis absorption and fluorescence spectra of **5a** (—) and **6** (- - -) in dichloromethane.

No distances typical for $\pi-\pi$ interactions are found between the extended aromatic diazadibenzoperylene surfaces as they are within a distance of about 10 Å. This might be a consequence of electrostatic repulsion of the charged π-systems, which might also be responsible for the tilted arrangement of the molecules in the stacks. The tetrafluoroborate anions are located between the layers in proximity to the positive charges at the nitrogen atoms. It therefore seems that the packing of the molecules in the crystal is mainly controlled by electrostatic ionic interactions.

Optical and Electrochemical Properties. The UV/vis absorption spectra of diazadibenzoperylenes **5a**,**b** are characterized by intense S_0-S_1 absorption bands located at $\lambda = 497 \pm 1$ nm (0−0 vibronic transition) and $\lambda = 465 \pm 1$ nm (first vibronic progression) in dichloromethane. The fluorescence emission spectra are close mirror images of the absorption spectra and display maxima at $\lambda = 514 \pm 2$ nm. No effect of the different phenoxy substituents on the optical absorption and fluorescence properties are found for compounds **5a**,**b**. Upon alkylation of the two nitrogens, an additional shoulder appears in the UV/vis absorption spectrum of **6** at the long-wavelength side of the S_0-S_1 transition leading to a bathochromically shifted fluorescence ($\lambda_{max} = 545 \pm 2$ nm) with a well-defined vibronic progression (Figure 3). The fluorescence quantum yields Φ_F are 0.75 ± 0.05 for the compounds **5a**,**b** and 0.50 ± 0.05 for **6**.

The cyclic voltammograms (CV) of diaza ligands **5a**,**b** show one reversible wave in the reductive cycle between −1.70 and −1.80 V (vs Fc/Fc$^+$), where reduction to the radical anions $\mathbf{5}^{\bullet-}$ occurs (Figure 4A). Oxidation is irreversible and accompanied by adsorption of the oxidized species on the platinum electrode surface. Repeated oxidation cycles lead to the growth of a film on the electrode as indicated by an increase in current with each scan (Figure 5A). Characterization of the coated electrode in a monomer-free electrolyte reveals multiple redox couples in the CV, suggesting the formation of an electroactive polymer of unknown chemical structure (Figure 5B).

For diazadibenzoperylenium dications (**6**), two reversible waves are observed at significantly higher electrode potentials than for **5a**,**b** in the reductive cycle, which suggest the reduction of **6** to the neutral antiaromatic π-system **7** via a radical cationic intermediate.



In the oxidative cycle, an additional reversible oxidation to the radical trication is possible, because **6**, in contrast to **5**, does not contain lone pairs of electrons at the nitrogen atoms that are susceptible to adsorption at the electrode surface and facile irreversible oxidation (Figure 4B).

Coordination Properties. The suitability of diaza ligand **5a** as a supramolecular building block was evaluated by complexation experiments in chloroform and tetrachloromethane with highly soluble Brönsted and Lewis acids, i.e., 3,4,5-tridodecyloxybenzoic acid (TBA) and zinc tetraphenylporphyrin (ZnTPP) (Scheme 2). For each experiment, changes in the environment of the

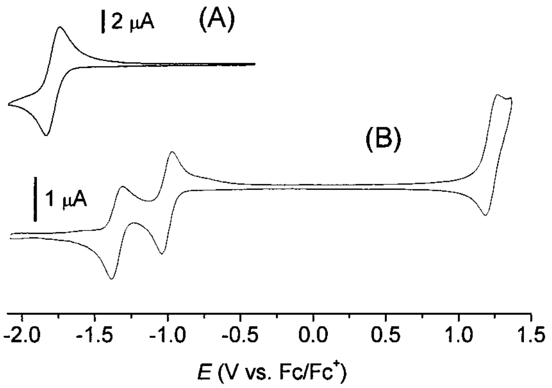


Figure 4. Cyclic voltammogram of **5a** (A) and **6** (B) in dichloromethane (sweep rate 100 mV s^{-1}).

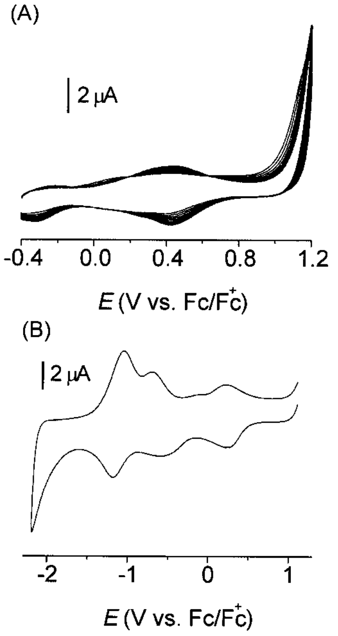
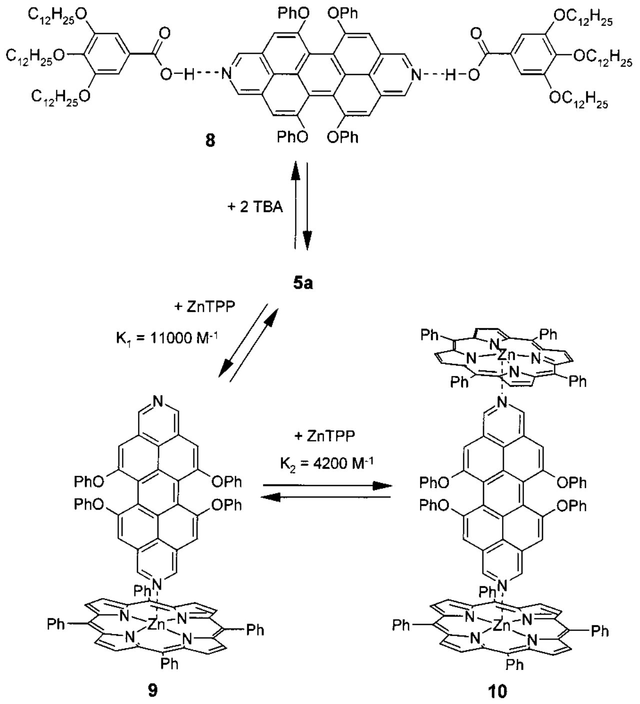


Figure 5. (A) Cyclic voltammograms of repeated oxidation scans for **5a** in dichloromethane indicating the growth of an electroactive film on the platinum electrode. (B) Characterization of the electroactivity of the adsorbed film in a monomer-free electrochemical cell by cyclic voltammetry (sweep rate 100 mV s^{-1}).

diazadibenzoperylene ligand (= host) were monitored upon addition of the binding partner (= guest) by ^{1}H NMR spectroscopy and from the titration curves binding constants[15] were calculated by nonlinear regression analysis under the assumption of two independent binding events. Complexation of **5a** with TBA in $CDCl_3$ results in a very small change of the chemical shift of the α-protons next to the complexing nitrogen atoms from $\delta = 9.22$ to 9.28 ppm. From the binding isotherm a microscopic binding constant K of 140 M^{-1} is obtained (Figure 6a).[15] More pronounced changes in the chemical shift of the α-proton from $\delta = 9.22$ (free ligand) to 2.90 ppm (calculated for fully coordinated ligand) were observed when **5a** was titrated with ZnTPP in $CDCl_3$ giving a binding constant K of 1500 M^{-1} (Figure 6b). The same value was obtained when the shift of the more distant diazadibenzoperylene γ-proton was evaluated which still receives a substantial shielding from 7.55 ppm (free) to 5.90 ppm (fully coordinated). Clearly, these large upfield shifts are not a result of the coordination of Lewis acidic metal centers but due to the coordination of the diaza ligand within the inner cone of the porphyrin ring current, giving unambiguous proof of the sandwich complex structure **10** suggested in Scheme 2.

Scheme 2



If the same NMR titration experiment is carried out in the less polar solvent CCl_4, an increase of the binding constant K to 3900 M^{-1} is observed that indicates a notable electrostatic contribution for the metal–ligand coordination as expected from crystal field theory. The latter self-assembly process that leads to a double-decker 2:1 complex (Scheme 2) could also be verified by a UV/vis titration experiment in tetrachloromethane operating within a different concentration range. Here, ZnTPP was selected as the host and pronounced changes of the porphyrin Q-bands upon addition of **5b** (Figure 7) could be evaluated applying the whole data set in a global fitting procedure.[16] Owing to the large number of experimental data points given for UV/vis spectra this experiment allowed us to extract the individual binding constants for the formation of a 1:1 complex between **5a** and ZnTPP ($K_1 = 1.1 \times 10^4$ L mol^{-1}) and the subsequent formation of the 1:2 double sandwich complex ($K_2 = 4.2 \times 10^3$ L mol^{-1}).[16] From the functional point of view, it is noteworthy that the photoluminescence of the diazadibenzoperylene fluorophore is completely quenched upon complexation of the zinc porphyrins, which is probably a result of a photoinduced electron-transfer process.[17]

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[15] All titration experiments were evaluated by assuming two independent receptor sites for diazadibenzoperylene **5a** and a negligible self-association of the guests TBA and ZnTPP within the investigated concentration range. All given binding constants are "microscopic" binding constants for individual binding events between two species. Owing to the well-known dimerization of carboxylic acids we note that the assumption of negligible self-association is critical in the case of TBA whereas for ZnTPP self-aggregation could be ruled out in the given concentration range by concentration-dependent UV/Vis absorption spectra. For a review about the coordination chemistry of metalloporphyrins, see: Wojaczynski, J.; Latos-Grazynski, L. *Coord. Chem. Rev.* **2000**, *204*, 113.

[16] SPECFIT/32 for Windows 95/98 & NT 4.0/2000 from Spectrum Software Associates: Marlborough, MA, 2000–2001.

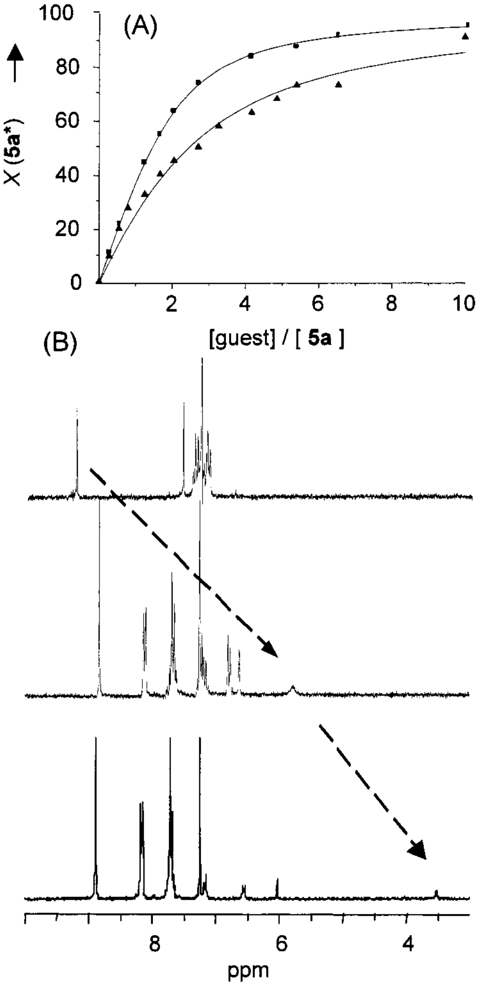

Figure 6. (A) Saturation plot showing the amount (%) of complexed aza receptor sites X (**5a***) for titration experiments with ZnTPP (squares) and TBA (triangles) in $CDCl_3$. (B) Three selected ^1H NMR spectra for the titration of **5a** with ZnTPP in $CDCl_3$. The arrows indicate the change in chemical shift of the protons α to the coordinating nitrogens from $\delta = 9.22$ (first spectrum without ZnTPP) to 3.53 ppm (third spectrum with a 10-fold excess of ZnTPP).

Conclusions

New functional supramolecular building blocks **5a**,**b** based on core-substituted diazadibenzoperylene dyes could be synthesized in four steps from tetrachloroperylenebisanhydride **1** in an overall yield of 16%. These dyes exhibit favorable optical (strong absorption, yellow emission with high quantum yield) and electrochemical (reversible reduction) properties as well as an extremely high solubility that enables self-assembly processes to be carried out over a wide concentration range. Complexation studies of the diazadibenzoperylene ligands to carboxylic acids and zinc porphyrins proved their suitability for the design of novel functional supramolecular architectures such as double decker sandwich complexes with metalloporphyrins (**10**), metallacycles,[6] as well as liquid crystals.[7]

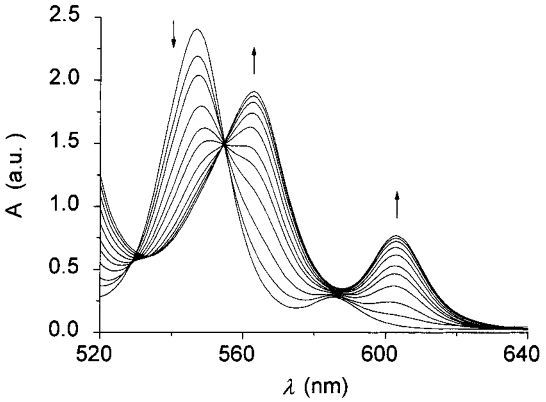

Figure 7. UV/vis titration of ZnTPP with **5a**. The arrows indicate the spectral changes of the porphyrin Q-bands upon addition of ligand **5a**.

Experimental Section

Materials and Methods. Solvents and reagents were purified and dried according to standard procedures.[18] 3,4,5-Tridodecyloxybenzoic acid,[19] *trans*-$[Pd(PPh_3)_2][(OTf)_2]$,[20] and zinc tetraphenylporphyrin (ZnTPP)[21] were synthesized according to the literature. 1,6,7,12-Tetrachloroperylene-3,4:9,10-tetracarboxylic acid bisanhydride[22] was donated by BASF AG. The solvents for spectroscopic studies were of spectroscopic grade and used as received. Fluorescence spectra were measured on a calibrated fluorometer in 1 cm quartz cells. All fluorescence spectra were corrected. Fluorescence quantum yields were determined relative to fluorescein in 0.1 N NaOH ($\Phi_R = 0.9$)[23] by the optically dilute method[24] ($A \leq 0.05$) in dichloromethane. Cyclic voltammetry was performed in a three-electrode single-compartment cell with dichloromethane as solvent (5 mL): Working electrode: platinum disk; counter electrode: platinum wire; reference electrode: Ag/AgCl. All potentials were internally referenced to the Fc/Fc^+ couple. The solutions were purged with argon prior to use. The supporting electrolyte was 0.1 M $[Bu_4N][PF_6]$, which was recrystallized twice from ethanol/water and dried in a high vacuum.

NMR Titration Experiments. All NMR titrations were performed at a constant diazadibenzoperylene receptor (= host) concentration of 7 mmol L^{-1} **5a** for the titration with TBA and of 3 mmol L^{-1} **5a** for the titration with ZnTPP in $CDCl_3$ at a temperature of 298 K. Aliquots of a guest solution containing 35 mmol L^{-1} of TBA and 15 mmol L^{-1} of ZnTPP, respectively, were subsequently added to an NMR tube containing an initial volume of 350 μL of the **5a** host solution. After each addition, a spectrum was recorded. For the titration of **5a** with ZnTPP in CCl_4, a special NMR tube with a sealed capillary containing deuterated acetone for lock-in was used. The experiment was carried out in the same way as described above with concentrations of 1.2 mmol L^{-1} (**5a**) and 3.7 mmol L^{-1} (ZnTPP) and a starting host volume of 350 μL. The binding constants were evaluated by nonlinear least-squares regression analysis from the change in chemical shift of the diazadibenzoperylene Hα protons.[13]

UV/vis Titration Experiments. The titration was performed at 5×10^{-4} mol L^{-1} constant ZnTPP (= host) concen-

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tration in CCl_4 at 298 K. Aliquots of the guest solution containing 2×10^{-3} mol L^{-1} of **5a** and 5×10^{-4} mol L^{-1} of ZnTPP were subsequently added to a cell (optical path length $d = 0.1$ cm) containing an initial volume of 100 μL of ZnTPP host solution. After each addition, a spectrum was recorded. The association constant was evaluated in a 1:2 model by a global nonlinear regression analysis taking into consideration the whole set of available spectral data between 520 and 640 nm.[16]

Crystal structure analysis of 6: $C_{56}H_{46}B_2F_8N_2O_4$, $M_r = 984.60$, monoclinic, space group $P2_1/n$ (no.14), $a = 12.8868(16)$ Å, $b = 21.825(5)$ Å, $c = 17.688(2)$ Å, $\beta = 99.743(14)°$, $V = 4903.2(14)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.334$ Mg m^{-3}, μ(Mo Kα) = 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 Kα radiation ($\lambda = 0.710\ 73$ Å, $2\theta_{max} = 51.94°$, $2\theta_{min} = 4.08°$); scanmodus rotation. The structure was solved by direct methods (SHELXS 97)[25] refinement on F^2 using the full-matrix least-squares-method (SHELXL 97).[26] 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 using 10 and 12 fluorine split sets, respectively, but the exact positions of the fluorine atoms could not be determined.[27] Crystallographic data (excluding structure factors) for the structure reported in this Chapter 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 CB21EZ, U.K. (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).[5a]

***N,N′*-Dibenzyl-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic Acid Bisimide (2a).** A suspension of 1,6,7,-12-tetrachloroperylene-3,4:9,10-tetracarboxylic acid bisanhydride **1** (7.95 g, 15.0 mmol) and benzylamine (8.03 g, 8.2 mL, 75.0 mmol) in propionic acid (100 mL) was stirred under reflux for 8 h. The product was isolated by filtration and washed with saturated $NaHCO_3$ and H_2O and then dried at 100 °C in vacuo. The product is sufficiently pure for further reactions but contains small amounts of pentachloroperylenebisimide and perylenemonoimide monoanhydride according to mass spectrometry: yield 9.70 g (91%); mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.69 (s, 4H), 7.55 (m, 4H), 7.36−7.27 (m, 6H), 5.41 (s, 4H); UV/vis (CH_2Cl_2) λ_{max} nm (ϵ, mol^{-1} dm^3 cm^{-1}) 520 (34 800), 487 (24 600), 427 (11 100), 270 (26 300); fluorescence (CH_2Cl_2) λ_{max} 551 nm; MS (FD, 8 kV) 708 (M$^+$). Anal. Calcd for $C_{38}H_{18}Cl_4N_2O_4$ (708.4): C, 64.43; H, 2.56; N, 3.95. Found: C, 63.49; H, 2.57; N, 3.74.

***N,N′*-Dibutyl-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic Acid Bisimide (2b).** As described for **2a** bisanhydride **1** (17.7 g, 33.4 mmol) and butylamine (9.8 g, 134 mmol) were reacted in propionic acid (200 mL) to afford 17.9 g (84%) of **2b**: mp >300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS) δ 8.68 (s, 4H), 4.22 (t, 4H), 1.74 (m, 4H), 1.49 (m, 4H), 1.00 (t, 6H); MS (FD, 8 kV) 640 (M$^+$). Anal. Calcd for $C_{32}H_{22}Cl_4N_2O_4$ (640.4): C, 60.02; H, 3.46; N, 4.37. Found: C, 59.32; H, 3.16; N, 3.99.

***N,N′*-Dibenzyl-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxylic Acid Bisimide (3a).** Perylene bisimide **2a** (7.08 g, 10.0 mmol), phenol (4.70 g, 50.0 mmol), and K_2CO_3 (5.52 g, 40.0 mmol) were stirred under argon in NMP (150 mL) at 130 °C for 16 h. The reaction mixture was poured into 1 N HCl (500 mL) and stirred for 1 h. The precipitate was collected, washed thoroughly with H_2O and MeOH, and dried. Purification was accomplished by dissolving the crude product in CH_2Cl_2 and precipitation by MeOH followed by chromatography on SiO_2 with CH_2Cl_2: yield 6.60 g (70%); mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.20 (s, 4H), 7.45 (m, 4H), 7.29−7.18 (m, 14H), 7.10 (m, 4H), 6.93 (m, 8H), 5.29 (s, 4H); UV/vis (CH_2Cl_2) λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1}) 575 (51 400), 536 (32 200), 446 (18 500), 284 (49 400), 264 (45 300); fluorescence (CH_2Cl_2) λ_{max} = 606 nm; MS (FD, 8 kV) 938 (M$^+$). Anal. Calcd for $C_{62}H_{38}N_2O_8$ (938.3): C, 79.31; H, 4.08; N, 2.98. Found: C, 79.24; H, 4.39; N, 3.33.

***N,N′*-Dibenzyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)perylene-3,4:9,10-tetracarboxylic Acid Bisimide (3b).** Prepared from perylene bisimide **2a** (7.08 g, 10.0 mmol), 4-*tert*-butylphenol (7.50 g, 50.0 mmol), K_2CO_3 (4.83 g, 35.0 mmol), and NMP (150 mL) in the same way as described for **3a** but with stirring at 140 °C for 8 h: yield 8.10 g (69%); mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.23 (s, 4H), 7.44 (m, 4H), 7.30−7.19 (m, 14H), 6.81 (d, ^3J(H,H) = 8.8 Hz, 8H), 5.30 (s, 4H), 1.29 (s, 36H); UV/vis (CH_2Cl_2) λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1}) 582 (49 300), 542 (29 700), 453 (18 100), 286 (48 600), 266 (46 100); fluorescence (CH_2Cl_2) λ_{max} 614 nm; MS (MALDI-TOF, dithranol) 1162.6 (M$^+$). Anal. Calcd for $C_{78}H_{70}N_2O_8$ (1163.4): C, 80.53; H, 6.06; N, 2.41. Found: C, 80.41; H, 6.13; N, 2.29.

***N,N′*-Dibutyl-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxylic Acid Bisimide (3c).** Prepared from perylene bisimide **2b** (8.30 g, 13.0 mmol), phenol (5.36 g, 57.0 mmol), K_2CO_3 (5.52 g, 40.0 mmol), and NMP (150 mL) as described for **3a**: yield 6.0 g (53%); mp >300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS) δ 8.18 (s, 4H), 7.26 (t, 8H), 7.10 (t, 4H), 6.93 (d, 8H), 4.10 (t, 4H), 1.65 (m, 4H), 1.39 (m, 4H), 0.93 (t, 6H); UV/vis (CH_2Cl_2) λ_{max}, nm 570, 532, 444, 284, 264; MS (MALDI-TOF, dithranol) 870.3 (M$^+$). Anal. Calcd for $C_{56}H_{42}N_2O_8$ (871.0): C, 77.23; H, 4.86; N, 3.22. Found: C, 77.10; H, 4.90; N, 3.10.

***N,N′*-Dibutyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)perylene-3,4:9,10-tetracarboxylic Acid Bisimide (3d).** Prepared from perylene bisimide **2b** (3.20 g, 5.0 mmol), 4-*tert*-butylphenol (3.3 g, 22.0 mmol), K_2CO_3 (2.1 g, 15.0 mmol), and NMP (50 mL) in the same way as described for **3a** but with stirring at 140 °C for 8 h: yield 3.0 g (56%) mp > 300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS) δ 8.22 (s, 4H), 7.23 (d, 8H), 6.83 (d, 8H), 4.11 (t, 4H), 1.66 (m, 4H), 1.36 (m, 4H), 1.29 (s, 36H), 0.93 (t, 6H); MS (MALDI-TOF, dithranol) 1094.7 (M$^+$). Anal. Calcd for $C_{72}H_{74}N_2O_8$ (1095.4): C, 78.95; H, 6.81; N, 2.56. Found: C, 78.60; H, 6.96; N, 2.36.

5,6,12,13-Tetraphenoxy-1,3,8,10-tetrahydro-2,9-dibenzyl-2,9-diazadibenzo[*cd*,*lm*]perylene (4a). $AlCl_3$ (7.48 g, 56 mmol) and $LiAlH_4$ (2.13 g, 56 mmol) were added to dry THF (300 mL) under argon and with cooling with an ice bath. The cooling bath was removed, and perylene bisimide **3a** (6.56 g, 7 mmol) was added in small portions. The mixture was stirred at 35 °C for 6 h, poured into cold 0.3 N hydrochloric acid (1.4 L), and stirred for 1 h. The precipitate was suction filtered, washed with H_2O, and dried. It was suspended in methanol (200 mL), and 1 N NaOH (50 mL) was added to precipitate the yellow amine **4a**, which was collected, washed to neutral, dried, and purified by MPLC chromatography on Si60 (CH_2Cl_2/MeOH 97:3): yield 4.20 g (68%); mp 252 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ 7.34−7.21 (m, 10H), 7.16 (t, ^3J(H,H) = 8.0 Hz, 8H), 6.97 (tt, J(H,H) = 7.4, 1.1 Hz, 4H), 6.82 (md, ^3J(H,H) = 8.6 Hz, 8H), 6.80 (s, 4H), 3.82 (s, 8H), 3.71 (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C) δ 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) λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1}) 453 (26 200), 429 (22 100), 381 (5200), 360 (3700), 298 (57 000), 259 (31 000); fluorescence (CH_2Cl_2) λ_{max} = 486 nm; MS (FD, 8 kV) 882 (M$^+$). Anal. 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.

5,6,12,13-Tetra(4-*tert*-butylphenoxy)-1,3,8,10-tetrahydro-2,9-dibenzyl-2,9-diazadibenzo[*cd*,*lm*]perylene (4b). Prepared from perylene bisimide **3b** (3.00 g, 2.58 mmol), $AlCl_3$ (2.87 g, 20.0 mmol), $LiAlH_4$ (0.78 g, 20.5 mmol), and THF (100 mL) in the same way as described for **4a**: yield 1.55 g (60%);

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mp 195 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ 7.34 (m, 4H), 7.30 (m, 4H), 7.24 (m, 2H), 7.14 (d, ^3J(H,H) = 9.0 Hz, 8H), 6.80 (s, 4H), 6.72 (d, ^3J(H,H) = 9.0 Hz, 8H), 3.84 (s, 8H), 3.72 (s, 4H), 1.27 (s, 36H); UV/vis (CH_2Cl_2) λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1}) 458 (25 400), 434 (21 500), 363 (4300), 304 (53 400), 264 (37 000); fluorescence (CH_2Cl_2) λ_{max} 494 nm; MS (MALDI-TOF, dithranol) 1106.8 (M^+). Anal. Calcd for $C_{78}H_{78}N_2O_4$ (1107.5): C, 84.59; H, 7.10; N, 2.53. Found: C, 84.56; H, 7.24; N, 2.46.

5,6,12,13-Tetraphenoxy-1,3,8,10-tetrahydro-2,9-dibutyl-2,9-diazadibenzo[*cd,lm*]perylene (4c). Prepared from perylene bisimide **3c** (3.48 g, 4.0 mmol), $AlCl_3$ (1.26 g, 9.4 mmol), $LiAlH_4$ (1.07 g, 28.3 mmol), and THF (30 mL) in the same way as described for **4a**, but MPLC was carried out with toluene/ethyl acetate (7:3) as eluent: yield 1.6 g (50%); mp 147 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS) δ 7.16 (m, 8H), 6.96 (m, 4H), 6.84−6.82 (m, 12H), 3.79 (s, 8H), 2.52 (t, 4H), 1.55 (m, 4H), 1.32 (m, 4H), 0.89 (t, 6H); UV/vis (CH_2Cl_2) λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1}) 452 (24 800), 430 (20 600), 362 (3700), 300 (55 500), 258 (30 600); MS (MALDI-TOF, dithranol) 814.4 (M^+). Anal. Calcd for $C_{56}H_{50}N_2O_4$ (815.0): C, 82.53; H, 6.18; N, 3.44. Found: C, 82.40; H, 6.30; N, 3.40.

5,6,12,13-Tetraphenoxy-2,9-diazadibenzo[*cd,lm*]perylene (5a). A mixture of **4a** (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 MPLC chromatography on Si60 (CH_2Cl_2/MeOH 97:3), **3** was isolated as a bright red solid: yield 1.00 g (48%); mp 273 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ 9.21 (s, 4H), 7.52 (s, 4H), 7.34 (t, ^3J(H,H) = 7.6 Hz, 8H), 7.18 (m, 4H), 7.13 (md, ^3J(H,H) = 7.6 Hz, 8H); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ 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) λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1}) 496 (62 300), 465 (34 900), 307 (22 500), 294 (21 800), 270 (47 000); fluorescence (CH_2Cl_2) λ_{max} = 511, 544 nm; fluorescence quantum yield ($CHCl_3$) $\Phi_F = 0.75$; MS (EI) 696 (M^+). Anal. 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.

5,6,12,13-Tetra(4-*tert*-butylphenoxy)-2,9-diazadibenzo-[*cd,lm*]perylene (5b). Prepared from **4b** (0.46 g, 0.42 mmol), 44 mg Pd/C (10% Pd), and diphenyl ether (20 mL) with stirring at 170 °C (5 h) in the same way as described for **5a**: yield 0.27 g (56%); mp 285 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) δ 9.18 (s, 4H), 7.48 (s, 4H), 7.29 (d, ^3J(H,H) = 8.4 Hz, 8H), 6.99 (d, ^3J(H,H) = 8.4 Hz, 8H), 1.33 (s, 36H); UV/vis (CH_2Cl_2) λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1}) 498 (61 200), 466 (35 800), 320 (23 600), 271 (49 900); fluorescence (CH_2Cl_2) λ_{max} = 515, 547 nm; fluorescence quantum yield ($CHCl_3$) $\Phi_F = 0.75$; HR-MS (EI) calcd *m/z* for $C_{64}H_{60}N_2O_4$ 920.4554, found 920.4554. Anal. Calcd for $C_{64}H_{60}N_2O_4 \cdot 0.5H_2O$ (930.2): C, 82.64; H, 6.61; N, 3.01. Found: C, 82.61; H, 6.58; N, 3.02.

5,6,12,13-Tetraphenoxy-2,9-dibutyl-2,9-diazadibenzo-[*cd,lm*]perylenium Bis(tetrafluoroborate) (6). A mixture of 5,6,12,13-tetraphenoxy-1,3,8,10-tetrahydro-2,9-dibutyl-2,9-diazadibenzo[*cd,lm*]perylene **4c** (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 and filtered, and H_2O (15 mL) and HBF_4 (1 mL of a 50% aqueous solution) were added to give a brown precipitate that 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 to give an orange crystalline solid: yield 0.25 g (51%); mp 272−275 °C dec; ^{1}H NMR (500 MHz, acetone-d_6, 25 °C, δ = 2.04 ppm) δ 9.92 (s, 4H), 8.03 (s, 4H), 7.50 (t, ^3J(H,H) = 7.9 Hz, 8H), 7.35 (t, ^3J(H,H) = 7.5 Hz, 4H), 7.30 (d, ^3J(H,H) = 7.8 Hz, 8H), 5.18 (t, ^3J(H,H) = 7.3 Hz, 4H), 2.29 (m, 4H), 1.50 (m, 4H), 0.96 (t, ^3J(H,H) = 7.3 Hz, 6H); ^{13}C NMR (126 MHz, acetone-d_6, 25 °C) δ 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) λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1}) 502 (55 000), 469 (35 200), 367 (15 500), 335 (22 300), 301 (64 700), 260 (51 800); fluorescence (CH_2Cl_2) λ_{max} = 532, 574 nm; fluorescence quantum yield ($CHCl_3$) $\Phi_F = 0.50$. Anal. 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.

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