2,9-Diazadibenzoperylene and 2,9-Dimethyldibenzoperylene-1,3,8,10-tetratriflates: Key to Functionalized 2,9-Diazaperopyrenes

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Abstract: The synthesis of 2,9-diaza-1,3,8,10-tetratriflate-dibenzoperylene (DDP 3a) and corresponding 2,9-dimethyl-1,3,8,10-tetratriflate-dibenzoperylene (DBP 3b) has been developed at multigram scale via reduction of one of the industrially most important high-performance dyes, perylene-3,4,9,10-tetracarboxylic diimide (PTCDI), and of the corresponding dihydroxy peropyrenequinone precursor. The focus of this paper is on the reactivity pattern of 3a as key intermediate towards highly functionalized 2,9-diazadibenzoperylenes (DDPs) obtained via catalytic substitution of four triflate by aryl, heteroaryl, alkyl, aminyl, and O-phosphoryl substituents. The influence of electron-donating substituents (OSiMe3, OPT-Bu2, N-piperidinyl), electron-withdrawing (OTf, 3,5-bis-trifluoromethyl-phenyl), and of electron-rich π-conjugated (2-thienyl, 4-tert-butylphenyl, trimethylsilyl-ethyl) substituents on optoelectronic and structural properties of these functionalized DDPs has been investigated via XRD analyses, UV/Vis, PL spectroscopy, and by electroanalytical CV. These results were correlated to results of DFT and TD-DFT calculations. Thus, functionalized DDPs with easily tunable HOMO and LUMO energies and gap became available via a new and reliable synthetic strategy starting from readily available PTCDI.

Introduction

Polycyclic (hetero)aromatic hydrocarbons (PAHs) are a versatile class of organic functional molecules investigated for their potential application in a number of technologies, such as organic photovoltaic devices (OPVs), organic field-effect transistors (OFETs) and energy storage applications.[1–12] Vast synthetic methodologies of their functionalization allow tailoring of their structural and optoelectronic properties. E.g., for the class of tetraazaperopyrenes (TAPP) related to our 2,9-diazadibenzoperylenes, DDPs an elaborate multi-step synthesis protocol was established in recent years.[11,12]

The probably most extensively studied and applied class of PAHs is derived from perylene-3,4,9,10-tetracarboxylic diimide (PTCDI), and of the corresponding dihydroxy peropyrenequinone precursor. The family of diazadibenzoperylenes (Figure 1) can be rationalized simply as products of PTCDI carbonyl group reduction. Nevertheless, only few reports of substituted or unsubstituted DDPs are known despite their structural relation to the archetypical PDIs.[16,17] The synthesis of DDPs was previously described in a two-step procedure via complete reduction of PTCDIs imide carbonyl groups to CH functionalities, subsequently followed by oxidative aromatization to form unsubstituted and poorly soluble DDP.[18] The low solubility of unsubstituted DDP is a drawback with respect to its further functionalization. A simpler approach to unsubstituted DDP involves naphthalene and triazine as starting materials.[19] Previous studies on DDPs demonstrated their functionality as sigma-donor ligands in tetranuclear Pd4+ and Pt4+ metallacycles and macromolecular systems.[20] Other studies investigated the binding affinities of cationic N-alkylated DDPs to nucleotides,[38] their intercalation with...
DNA and as sensors in enantioselective reactions. Recently, their photophysical properties were investigated in detail.

A second structurally related class of PAHs are dibenzo-perylenes (DBPs, Figure 1) with their 26 $\pi$-electron system, also known as peropyrenes. Peropyrenes can be formally described as C–H analogues of DDPS and are currently investigated as singlet fission material. It was stated that a good method to introduce substituents onto peropyrene is still lacking.

We also demonstrated a reductive silylation and introduction of four replaceable and versatile triflate substituents. We turned out to undergo not only Suzuki-Miyaura coupling with a larger set of aryl boronic acids and without need of using a reducing agent due to its easy handling on a multigram scale. Starting material 1b was synthesized via an oxidative coupling of 2-methyl 3-hydroxy-1-phenalenone in a potassium hydroxide melt modifying similar oxidative reactions. This oxidative coupling followed by reductive triflylation protocol allowed the introduction of other organic groups in 2,9- and 1,3,8,10-position of peropyrenes.

Peropyrene 2b was obtained via reduction of dihydroxy peropyrenequinone 1b using potassium graphite (C$_4$K) as reducing agent and trimethylsilylechloride (TMSCl) as trapping reagent. Overall, sodium in diglyme seems to be the preferred reducing agent due to its easy handling on a multigram scale. Orange solid 2a can be handled under aerobic atmosphere, however in solution and in presence of air and moisture, 2a is re-oxidized to starting material PTCDI, which is deposited as thin film on the inner glass surface of the flask, as is verified by IR spectroscopy (Figure S1). This selective aerobic reoxidation and deposition reaction can be used to fabricate pure and transparent PTCDI films from solution.

In the second step, 2a is activated and trimethylsilyl groups are replaced by triflyl groups. We obtained key intermediate 3a in 60% yield upon treating 2a with trifluoromethanesulfonic anhydride (Tf$_2$O) in the presence of equimolar amounts of N,N-dimethyl-4-aminopyridine (DMAP) as activating agent for Tf$_2$O (Scheme 2). N-Methylimidazole may also be used as a Tf$_2$O activating agent. A second method yielded 3a in 34% yield via reaction of Tf$_2$O with tetrabutylammonium salt 8 generated by desilylation of 2a with n-butyllithium (n-

**Syntheses and characterization of DDPS and DBPs**

Independently from Miyake’s tetravaloyl route we developed a protocol for reductive silylation and conversion of PTCDI into 1,3,8,10-tetrafrioated-2,9-diaza-peropyrene 3a (Scheme 2). Details are presented here. Triflate groups in key intermediate 3a tend to be more reactive and more versatile in their reaction patterns than pivaloate groups. They turned out to undergo not only Suzuki-Miyaura coupling with a larger set of aryl boronic acids and without need of using the latter in large molar excess. Furthermore, triflates are able to undergo Sonogashira cross-coupling reactions or direct uncatalyzed nucleophilic substitution reactions. And they could be installed not only in 1,3,8,10-tetrafrioated-2,9-diaza-peropyrene 3a but also in corresponding dimethyl-peropyrene 3b (Scheme 2).

Scheme 1 displays the first reductive functionalization step towards soluble tetralslaoxy-2,9-diaza-peropyrene 2a and 2,9-dimethyl-dibenzo-perylenes 2b. PTCDI (1a) is reduced using sodium in diglyme at 160°C at a 70:gram scale. The precipitating sodium salt of reduced PTCDI is reacted in situ with trimethylsilyl chloride forming highly soluble 2a in good yields of around 55%. Another synthetic route towards 2a was reported using n-butyllithium as reducing agent for PTCDI.
This method turned out to be the better one when 2b was desilylated by four equivalents of n-BuLi. Treatment of in situ forming and precipitating tetraalumium salt with TfO in diethyl ether yielded tetrafluoroborate DBP 3b in 54% yield. Careful handling of 3b is required since it decomposes rapidly in air at ambient light. The synthetic viability of PTCI derived tetralithium salt 8 in reactions with electrophiles is demonstrated by its use as synthon in the high-yield synthesis of tetraphosphinate 4, a potential bifunctional PONOP pincer ligand in 82% yield (Scheme 2).

Tetrafluoroborates 3a and 3b are versatile key intermediates in the synthesis of highly functionalized DDPs and DBPs. In this report we focus on the synthesis of DDPs, the functionalized DBP series is reported separately.[27] Three representative examples of functionalization reactions for DDP 3a are shown in Scheme 3. Firstly, Suzuki-Miyaura cross-coupling reactions were carried out using phenyl boronic acids (1.5 instead of 4.0 eq per functional group) and catalytic amounts of PdCl2(PPh3)2 (2.5 mol% per functional group) to obtain 1,3,8,10-tetraaryl DDPs 5a–5e. The yield for 5b is similar to previously reported applying tetrakis(triflate) with fourfold excess of boronic acid per functionality.[30] DDP 5a is a red soluble C60-PAH sublimable at temperatures >350 °C and 10−13 mbar. Noteworthy, we were able to provide a chromatography-free work-up of 5a–5d. Secondly, a representative Sonogashira reaction was carried out with trimethylsilylacetylene and catalytic amounts of PdCl2(Ph3P)2 (0.17 equiv) to produce 6 in 15% yield, a transformation not accessible via tetrakis(triflate) so far. Stoichiometric amounts of [n-Bu4NI] were added to the reaction in order to in situ substitute OTf moieties with iodine groups and for providing a superior reactivity compared to triflate in some cross coupling reactions. Desilylation of tetrathethyl derivative 6 will allow further modifications such as Glaser couplings or other cross-coupling, cycloaddition, or ring annulation reactions. Finally, we made use of the accessibility of triflate groups in 3a for uncatalyzed nucleophilic substitution reactions, again a strategy not available for less reactive tetrakis(triflate). In this respect, 3a was used in direct nucleophilic amination with piperidine to obtain 7. The substitution proceeds nearly instantaneously as observed by a color change to a purple solution. Air-sensitive, very electron-rich tetrapiperidyl derivative 7 was obtained in pure form by simply washing the crude solid with degassed water.

We obtained single crystals suitable for low-temperature X-ray crystallographic analysis of 2a, 2b, 3a, 4, 5b and 5c. Their molecular and lattice structures are presented in Figure 2 and Figure S7. All compounds adopt a highly planar central DPP conformation with only little deviation of atoms from the mean aromatic plane: av. 0.04 Å, 0.02 Å, and 0.05 Å for 2a, 3a, 3b, 4, 5b and 5c, respectively. 2a and 5c crystallize in triclinic space groups P1 with a slip stacked arrangement and with shortest inter-plane arene contacts of 3.39 Å and 3.49 Å, therefore exhibiting significant π–π interactions. 2b, 3b and 5b crystallize in monoclinic space groups P21/n, P21 and P21/n in a heringbone-like arrangement with similarly short distances of the aromatic planes (3.56 Å and 3.38 Å for 2b and 3b). 5b forms dimers with intra-dimer distances of 3.62 Å and inter-dimer distances of 3.78 Å, indicating a weaker interaction than that of 5c. 4 crystallizes in the orthorhombic space group.

![Scheme 3. Functionalization reactions of triflate 3a: (a) R–8(OH)2, (6.0 equiv), Pd[Ph2P(CH2)] (0.1 equiv), NaHCO3 (aq), Tol/ EtOH, 90 °C, 12 h–7 d; (b) trimethylsilylacetylene (6.0 equiv), PdCl2(Ph3P)2 (0.2 equiv), Cul (0.6 equiv), Bu4NI (6.0 equiv), DMF/ Et,N, rt, 3 h, 15%. (c) piperidine (17 equiv), DMSO, 90 °C, 20 h, 63%.

Figure 2. Molecular and packing structures of (a) 2b, (b) 3a, (c) 4 and (d) 5c. Hydrogen atoms and solvents molecules are omitted for clarity. Thermal ellipsoids are shown at 50% probability.]
P2,2,2 and exhibits no \( \pi \)-stacking due to four sterically demanding \( \text{OPt-Bu} \) groups.

All molecules reveal very similar C–C bond lengths of the DDP core ranging from 1.350(3) Å to 1.433(4) Å. On the basis of the C–C bond lengths between naphthalene subunits (C–C 1.47 Å, Figure S8), parent PTCDD is well described as two fused naphthalene units.\(^{32}\) Contrastingly, the investigated DDPs have shorter C–C bond lengths between the naphthalene subunits (1.42 Å). According to the bond length pattern, the aromaticity of the DDPs and DBPs \( 3b \) can be described according to Clar’s sextet model with the three axially located central benzene rings as Clar sextets (see Figure S8).\(^{35–36}\)

Figure 4 displays the UV/Vis and emission spectra of selected compounds in \( \text{CH}_2\text{Cl}_2 \). The influence of the 2,9-position (nitrogen versus carbon atom) is investigated for DDPs \( 2a \) and \( 3a \) and DBPs \( 2b \) and \( 3b \). Dyes 2 and 3 show pronounced vibronic progression fine structures with spacings of \( \approx 30 \) nm in the absorption and mirrored emission spectra typical for diazidabenzoylenes and dibenzopyrenes.\(^{29}\)

The emission maxima are bathochromically shifted for \( 2a \) and \( 3a \) compared to \( 2b \) and \( 3b \). The redshifted emission maxima and the larger Stokes shifts for DDPs (Table 1) indicate a more pronounced configurational change between the ground state and the excited state and higher reorganization energy loss between absorption and emission, possibly caused by the nitrogen-induced dipole momentum change upon excitation.

The introduction of electron-rich substituents in 1,3,8,10-position leads to an increased bathochromic shift of the absorption and emission maxima. The absorption maxima range from 455 nm for the electron-poor tetratristole \( 3a \) to 550 nm for the most electron-rich tetraperipropoyd substituted 7. Emission maxima range from 473 nm (\( 3a \)) to 583 nm (7). Both, absorption and emission spectra demonstrate the optical tunability of DDPs by functionalization of positions ortho to the nitrogen atoms. The vibronic structure is less pronounced for 4, 5 and 7. Contrastingly, 6 exhibits a pronounced vibronic fine structure and a small Stokes shift of 7 nm (253 cm\(^{-1} \)) indicating a more rigid aromatic backbone.

The addition of 5 vol-% trifluoroacetic acid (TFA) to a \( \text{CH}_2\text{Cl}_2 \) solution of \( 5a \) and \( 5e \) causes their protonation and a bathochromic shift of the emission (Figure S2, S3 and S4).

The electrochemical properties of structurally related \( 5a-5e \) were investigated by cyclovoltammetry and differential pulse voltammetry (Table 2, Figures 3 and S5). \( 5a \) exhibits two reversible reduction and oxidation waves, which are lower for \( 5c \) and \( 5d \) with more electron-withdrawing substituents. Compared to more electron-rich \( 5b \) and \( 5e \) the opposite trend is observed for the oxidation waves, indicating a strong influence of the 1,3,8,10-substituents on the LUMO energies of these DDP derivatives, in particular. Overall, the obtained experimental and calculated HOMO and LUMO energies (Table 2, Figure 5, Table S1) are in good agreement for \( 5a, 5b \) and \( 5e \) and confirm the trend for \( 5c \).

DFT calculations

The trends of absorption maxima (Figure 4) is supported by TD-DFT calculations at PBE0-D3(BJ)/def2-TZVPP level of theory (see Table S2-S15 for details). In all cases, the lowest-energy absorption band is correlated to a HOMO-LUMO (\( S_0 \) to \( S_1 \)) electronic transition. Furthermore, the influence of electron-withdrawing and electron-releasing substituents on the photo-

| Table 1. Summary of photophysical data.\(^{[a]}\) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Compound | \( \lambda_{\text{abs}, \text{max}} \) [nm] | \( \lambda_{\text{em}, \text{max}} \) [nm]\(^{[b]}\) | Stokes shift [cm\(^{-1} \)] | \( E_{\text{opt}} \) [eV]\(^{[c]}\) |
| 2a | 490 | 508 | 723 | 2.48 |
| 2b | 497 | 488 | 385 | 2.57 |
| 3a | 455 | 474 | 881 | 2.68 |
| 3b | 457 | 466 | 423 | 2.68 |
| 4 | 498 | 540 | 1562 | 2.44 |
| 5a | 500 | 517 | 1066 | 2.45 |
| 5a\(^{[2]}\) | 487 | 551 | 2385 | 2.36 |
| 5b | 497 | 528 | 1181 | 2.41 |
| 5c | 490 | 521 | 1214 | 2.45 |
| 5d | 502 | 538 | 1333 | 2.37 |
| 5e | 543 | 574 | 995 | 2.21 |
| 5e\(^{[2]}\) | 519 | 612 | 2928 | 2.15 |
| 6 | 522 | 592 | 253 | 2.36 |
| 7 | 550 | 583 | 1029 | 2.19 |

\( =[a] \) Solvent, \( \text{CH}_2\text{Cl}_2 \); [b] excitation wavelength 350 nm; [c] 5 vol-% TFA added; [d] determined from the intersection wavelength of normalized absorption and emission spectra.

![Figure 3. Cyclic voltammetry (solid line) and differential pulse voltammetry (dashed line) of 5b-5e. Measurements were performed in a saturated \( \text{CH}_2\text{Cl}_2 \) solution with 100 mM \( n\)-BuNPF\(_4 \) as electrolyte.](image-url)
physical and electroanalytical properties of 2–3 and 5–7 was rationalized. Molecular orbital diagrams are shown in Figure 5 and Figure S9.

The frontier Kohn-Sham orbitals and energies support our experimental observation that substituents in 1,3,8,10-position strongly influence the electronic properties. Both, HOMO and LUMO are delocalized over the DDP backbone and to some extent over the *ortho* substituents, as shown in Figure 5. This participation of the substituents to the frontier orbitals explains a strong effect on the optoelectronic properties of DDPs. The participation of the substituents to the frontier orbitals is especially pronounced for 2, 3, 5e, 6 and 7. The substituents in 6 are contributing via the conjugated triple bond π system, while in 2, 3 and 7 the oxygen and nitrogen atoms are directly contributing to the HOMO and LUMO coefficients of the aromatic system. As expected, electron-withdrawing substituents such as triflate (3a) or 3,5-bis (trifluoromethyl)phenyl (5c) lead to low-lying frontier orbitals, whereas electron-donating substituents such as 2-thienyl (5e) and piperidinyl (7) lead to energetically high-lying frontier orbitals. However, as observed for highly reactive triflates 3a,b, energetically low-lying HOMO and LUMO frontier orbitals do not guarantee any air stability as an energetically low-lying LUMO may be attacked by water as nucleophile while a high-lying HOMO is giving rise to oxygen sensitivity.

The influence of [N] versus [CMe] building blocks in 2,9 positions on the HOMO and LUMO energies (Table S1 and Figure S9) is calculated for the new title compounds and triflate key intermediates 3a and 3b. As expected sp² nitrogen atoms in the 2,9-position lead to a stabilization of the frontier orbitals. The same trend was reported for similar tetrasubstituted peropyrenes[27] and related 2,8-diazaperopyrenes, recently.[37]
Experimental Section

Methods and materials: All reactions were carried out under inert nitrogen atmosphere using Schlenk techniques if not mentioned otherwise. All reagents were purchased from commercial sources if not mentioned otherwise and were used without further purification. All solvents were dried and/or purified according to standard procedures and stored over 3 Å or 4 Å molecular sieves.

Procedure and materials

Absorption maxima ranging from 455 nm to 550 nm and emission maxima from 474 nm to 583 nm were correlated with absolute HOMO and LUMO levels and on the HOMO-LUMO gap, as rationalized via UV/Vis and PL spectroscopy, by CV and differential pulse voltammetry measurement. Cyclic voltammetry and differential pulse voltammetry measurements are carried out on a Rhd instruments TSC 1600 closed electrochemical workstation (working electrode: glassy carbon; counter electrode: platinum crucible; reference electrode: platinum wire) and were used for electrochemical analysis. The measurements were carried out at a concentration of 100 mmol/L of electrolyte and 5 mM sample.

Selected synthetic procedures: A detailed description of all preparative procedures and characterization of compounds is deposited in the Supporting Information.

Dihydroxyperopyrenequinone (1b): Naphthal anhydride (10.0 g, 50.5 mmol, 1.0 equiv), diethyl maleyl maleonate (26.0 g, 151.4 mmol, 3.0 equiv) and ZnCl2 (15.1 g, 111.0 mmol, 2.2 equiv) were stirred for 15 min at 25 °C and 5 h at 195 °C. The solidified orange product mixture was dissolved in NH4OH (5 % in H2O) and filtered. The red filtrate was acidified with hydrochloric acid, the yellow precipitate was filtered off and washed with H2O. Recrystallization from toluene yielded the product (7.75 g, 36.9 mmol, 73 %) as yellow needles. 1H NMR (300 MHz, CDCl3): δ = 8.43 (d, J = 6.5 Hz, 2H), 8.09 (dd, J = 8.0, 7.0 Hz, 2H), 7.68 (dd, J = 8.0, 7.0 Hz, 2H), 2.19 (s, 3H) ppm. 13C NMR (75 MHz, CDCl3): δ = 133.1, 131.9, 126.6, 113.1, 7.9 ppm. APCI-HRMS(−) (C19H14O): found (calc.) m/z 209.0608 (209.0608). This intermediate product, 3-hydroxy-2-methyl-1-phenalenylcarbone (7.5 g, 35.7 mmol) was purified according to literature and recrystallized from hot methanol and washed until the filtrate was colorless. The product was obtained as black solid (7.0 g, 16.8 mmol, 94 %). APCI-HRMS(−) (C19H14O): found (calc.) m/z = 417.1121 (417.1123).

2.9-Diaza-1,3,8,10-tetraakis(trimethylsilyl)oxazidopyreneylene (2a): PTCDI (71.3 g, 182.7 mmol, 1.0 equiv) and sodium (18.4 g, 270.6 mmol, 3.0 equiv) were stirred for 6 h at 160 °C. Trimethylsilyl chloride (140 mL, 6 equiv) was added in portions and the suspension stirred for 4 at room temperature and 3 h at 160 °C. All volatile compounds were removed in vacuo, the product was dissolved in CH2Cl2 (ca. 300 mL) and the solution was filtered. The solvent was removed in vacuo and the product was obtained via crystallization from toluene (68.6 g, 100.8 mmol, 55 %). 1H NMR (300 MHz, CDCl3): δ = 8.85 (d, J = 9.5 Hz, 4H), 8.28 (d, J = 9.5 Hz, 4H), 0.57 (s, 36H) ppm. 13C NMR (75 MHz, CDCl3): δ = 154.6, 134.4, 126.4, 124.3, 122.5 (CH (δ = 8.28 ppm), 112.0 (CH (δ = 8.65 ppm), 110.8, 0.9 (CH) ppm. FD-HRMS(−) (C36H34N4OS4): found (calc.) m/z = 680.23605 (680.23781). FTR: ν = 2955 (m), 2901 (w), 2853 (w), 1624 (m), 1584 (m), 1545 (s), 1485 (m), 1467 (w), 1396 (s), 12615 © 2021 The Authors. Chemistry - A European Journal published by Wiley-VCH GmbH
2.9-Dimethyl-1,3,8,10-tetraakis(triethylsilyloxy) dibenzoperylene (2b): 1b (2.5 g, 6.0 mmol, 1.0 equiv) and CαK (3.5 g, 25.9 mmol, 4.3 equiv) were suspended in 100 mL THF and stirred for 3 d at 55 °C and 8 h at 65 °C. Trimethylsilyl chloride (4.5 mL, 36.0 mmol, 6.0 equiv) was added slowly at room temperature and stirred over night at 60 °C. Volatile compounds were removed under reduced pressure, the remaining solid dissolved in CHCl₃ and filtered. The solution was filtered through a pad of silica gel and the product washed with pentane. The pure product was obtained as orange solid (0.92 g, 1.3 mmol, 22%). ¹H NMR (300 MHz, CDCl₃): δ = 9.01 (d, J = 9.5 Hz, 4H), 8.42 (d, J = 9.5 Hz, 4H), 2.59 (s, 6H), 0.41 (s, 36H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = 149.6 (COSiMe₃), 125.1, 123.7, 121.9 (CH), 120.4 (CH), 119.1, 13.2 (CH₂), 1.2 (SiMe₃) ppm. ²⁵Si NMR (99 MHz, CDCl₃): δ = 224 ppm. FD-HRMS (+) (C₂H₇O₂Si₃): m/z = 706.27735 (706.27861). FTIR: ν = 2955 (w), 2900 (w), 1546 (m), 1387 (m), 1365 (w), 1343 (w), 1304 (m), 1248 (m), 1221 (m), 1172 (m), 1145 (m), 1101 (m), 1034 (w), 915 (s), 838 (s), 787 (m), 756 (m), 705 (m), 691 (m), 657 (m), 568 (w), 457 (w) ppm. Elemental analysis for C₂H₇O₂Si₃: found (calc.): m/z = 706.27861, 706.27735. IR ν (CHCl₃): δ = 2880 (s), 2846 (s), 1561 (s), 1456 (s), 1394 (s), 1343 (m), 1294 (m), 1259 (m), 1197 (s), 1183 (s), 1162 (m), 1084 (s), 1034 (s), 1010 (s), 955 (m), 918 (m), 806 (m), 790 (w), 753 (m), 715 (s), 706 (s), 667 (s), 639 (m), 608 (m), 591 (m), 501 (s), 458 (m), 427 (m) ppm. UV/Vis (CHCl₃): δ = 498, 462, 434 nm. PL (CHCl₃): ox₃: λₜₐₜ = 450 nm: Eₜₐₜ = 0.32 V, Eₜₐₜ = 0.17 V, Eₜₐₜ = 0.75 V. Crystals for structure determination were obtained from diethyl ether.

2.9-Diaza-1,3,8,10-tetraphenyl-dibenzoperylene (3a) Method A: 2a (8.00 g, 11.7 mmol, 1.0 equiv) was dissolved in Et₂O (250 mL) and slowly treated with n-BuLi (2.75 M in hexane, 17.1 mL, 47.0 mmol, 4.0 equiv) at room temperature. TF₃O (7.90 mL, 132.2 g, 47.0 mmol, 4.0 equiv) was slowly added after 18 h at –78 °C (1.75 mL/h) and stirred for 1 d. The suspension was filtered and washed with THF. The remaining solid was extracted with chloroform and the product obtained after the removal of the solvent under reduced pressure as orange powder (3.66 g, 0.4 mmol, 34%). ¹H NMR (300 MHz, CDCl₃): δ = 9.50 (d, J = 9.0 Hz, 4H), 8.70 (d, J = 9.0 Hz, 4H) ppm. ¹³C NMR was not collected due to low solubility. ¹³C NMR (126 MHz, CDCl₃), δ = 120.2 ppm. FD-HRMS (+) (C₁₂H₁₀N₂O₂Si₃): m/z = 945.91762 (945.91643). IR ν = 2938 (m), 2890 (m), 2857 (m), 1685 (s), 1620 (m), 1585 (m), 1545 (m), 1466 (m), 1393 (m), 1349 (m), 1290 (m), 1259 (s), 1197 (s), 1183 (s), 1162 (m), 1084 (s), 1034 (s), 1010 (s), 955 (m), 918 (m), 806 (m), 790 (m), 753 (m), 715 (s), 706 (s), 667 (s), 639 (m), 608 (m), 591 (m), 501 (s), 458 (m), 427 (m) ppm. UV/Vis (CHCl₃): δ = 149.6, 498, 462, 434 nm. PL (CHCl₃ vs. Fc/Fc+): Eₜₐₜ = –0.32 V, Eₜₐₜ = 0.14 V, Eₜₐₜ = 0.17 V, Eₜₐₜ = 0.75 V. Crystals for structure determination were obtained from diethyl ether.

2.9-Diaza-1,3,8,10-tetraakis(3,5-bis(trifluoromethyl)phenyl)dibenzoperylene (5c): 3a (0.32 g, 0.35 mmol, 1.0 equiv) and Ph(PPh₃)₂ (0.05 g, 0.04 mmol, 0.15 equiv) were suspended in 8 mL toluene. 3,5-Bis(trifluoromethyl)phenylboronic acid (0.54 g, 2.1 mmol, 6.0 equiv) was dissolved in 4 mL ethanol and added with 2 mL degassed, saturated aqueous NaHCO₃ solution to the reaction mixture and stirred at 90 °C. After 12 h the reaction mixture was filtered through a pad of silica gel, solvent was stripped at reduced pressure and the residue was crystallized from CHCl₃/pentane and washed with n-pentane. 5c was obtained as red solid (0.14 g, 0.12 mmol, 35%). ¹H NMR (300 MHz, CDCl₃): δ = 9.47 (d, J = 9.5 Hz, 4H), 8.62 (d, J = 9.5 Hz, 4H), 8.49 (s, 8H), 8.14 (s, 4H) ppm. ¹³C NMR (300 MHz, CDCl₃): δ = 146.9, 136.3, 136.3, 133.7, 133.3, 133.2, 133.2, 132.1, 131.7, 129.1, 127.7, 126.6 ppm. ¹³C NMR (282 CDCl₃): δ = 62.6 (s) ppm. FD-HRMS (+) (C₂₇H₂₂NF₄): found (calc): m/z = 1176.2783 (1176.2748). IR ν = 3092 (w), 1581 (w), 1382 (m), 1316 (s), 1216 (s), 1287 (s), 1274 (s), 1265 (s), 1173 (s), 1134 (s), 1115 (s), 1082 (s), 995 (w), 900 (s), 873 (m), 848 (m), 796 (m), 750 (m), 699 (m), 682 (s), 646 (m), 581 (w), 560 (w), 505 (w), 444 (w), 408 (w) ppm. UV/Vis (CHCl₃): ox₃: λₜₐₜ = 500 nm: Eₜₐₜ = 0.32 V, Eₜₐₜ = 0.14 V, Eₜₐₜ = 0.17 V, Eₜₐₜ = 0.75 V. Crystals for structure determination were obtained from a toluene/pentane solution.
The authors declare no conflict of interest.

Keywords: diaziperopyrenes · organic dyes · peropyrenes · perylene diimide · reductive aromatization

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