Towards Nitrogen-Rich N-Heteropolycycles: Synthesis of Octaazaperopyrenes (OAPP)

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Abstract: Ortho substituted octaazaperopyrenes (OAPPs) are a new class of functional dyes characterized by their strong electron-accepting behavior. Herein, the synthesis, as well as the electrochemical and photo physical properties of an OAPP dye, is reported. The OAPP target was prepared via selective nucleophilic substitution at the peri position of a bay chlorinated tetraazapyrene by introduction of four amino-substituents. The resulting tetrainoperylene was reacted with different acyl chlorides and anhydrides to give the twisted bay chlorinated OAPP derivatives which were isolated in their reduced dihydro-form. The OAPP target could be obtained via a palladium catalyzed dehalogenation and a subsequent oxidation. The eightfold isosteric [CH—N] replacement within the peropyrene core structure results in a large decrease of the frontier orbital energies, rendering the target compound a potent oxidant while preserving the planarity of the aromatic core. The radical anion was obtained by reduction of the OAPP with KC8 and characterized by EPR spectroscopy. A general discussion of the number and location of [CH—N] replacements in peropyrene structures and their frontier orbital energies is provided.

Introduction

The use of functional dyes as electronic materials has led to a revival of the chemistry of polycyclic aromatic compounds.\[^{[1–7]}\] Interesting in their own right due to fine tunable photophysics and redox properties in solution, their properties as conducting solids has significantly driven this development.\[^{[8–9]}\] While there are nowadays many organic p-semiconducting materials with high charge carrier mobilities, which can be used for the OFET technology,\[^{[10–11]}\] the performance of n-semiconducting materials based on molecular compounds with electron acceptor properties remains to be improved.\[^{[12–13]}\] One strategy towards new electron acceptors is the isosteric replacement of CH-units by nitrogen atoms within the polycyclic aromatic cores, thus lowering the energies of the frontier orbitals, in particular the LUMOs.\[^{[14–16]}\] This approach has been extensively studied in acene chemistry and shown to convert the typical p-semiconducting materials into an n-semiconducting material.\[^{[6,17–20]}\]

The synthesis of N-heteroacenes has a long history. In pioneering studies by Hinsberg\[^{[21]}\] as well as Hepp and Fisher\[^{[22]}\], the first oligoaacenes were synthesized and characterized. The tetracenes which were obtained in the reduced form (NH-compounds) were easily oxidizable, a step which proved more challenging for condensed aromatics (e.g., dihydronaphthazine).\[^{[23–24]}\] The oxidation of larger azacenes with acidic dichromate generally results in the corresponding quinones\[^{[25]}\] which allows the synthesis of alkylated azacenes by a nucleophilic reaction with lithium acetylides and a subsequent full aromatization with SnCl4.\[^{[19,26–27]}\]

To date, many azapentacenes\[^{[28–30]}\] and larger acenes\[^{[31–33]}\] have been synthesized which are strong electron acceptors and exhibit n-semiconducting behavior.\[^{[5–6,14,17–18,34–35]}\] These studies have revealed that the position of the nitrogen atoms in the aromatic core plays an important role in influencing the semiconducting properties, electronic structure and molecular packing.\[^{[17–18,36]}\] Additionally, computational studies have been carried out to model the materials properties and to analyze the influence of the isosteric [CH—N] replacement.\[^{[19–16,20,37]}\]

We systematically investigated the chemistry and properties of tetraazaperopyrenes (TAPP) as electron accepting functional dyes which were found to possess similar electrochemical and photo physical properties but distinctly different reactivity compared to the extensively studied perylenediimides (PDIs).\[^{[38–51]}\] In contrast to the PDIs, the electron accepting character of the TAPP derivatives arises from the fourfold isosteric replacement [CH—N] and not the addition of strong electron withdrawing groups like the carboximide substituents.\[^{[44]}\] In this way, the strong electron accepting behavior and the resulting electronic materials properties are introduced into the aromatic core without changing the molecular shape.\[^{[38]}\]

In TAPP molecules, the electrophilic substitution of the parent compound (e.g., bromination) occurs solely in the ortho-position\[^{[44]}\] whereas the PDIs react in the bay-position.\[^{[22–25]}\] Numerous derivatives of the TAPP substituted in the “axial” 2, 9-positions\[^{[26,42]}\] and in the ortho-positions\[^{[43–44,36–37]}\] have been
studied for more than a decade which has provided detailed insight with regard to their electronic and photophysical properties and allows reliable predictions of their behavior.

Additionally, we recently developed a synthetic approach to functionalize the bay-position which made the bay chlorinated and perhalogenated TAPPs accessible,[48–50] while the planarity of the aromatic core is lost due to the steric pressure. Finally, perhalogenation of the TAPP core (Scheme 1) leads to further reduction of the LUMO energy and improved electron acceptor properties, rendering radical anions and dianionic species isolable.[56]

In this work, we expand the concept of the isosteric [CH→N] replacement to further reduce the HOMO and LUMO energies of a polycyclic aromatic system[56] without addition of acceptor substituents.[59] The aim is an access to a powerful electron acceptor, without significant changes in the molecular shape of the molecules, in particular, loss of the planarity of the aromatic core.[57] Based on the peropyrene scaffold as point of reference, we developed the synthesis of a novel N-atom rich octaazaperopyrene, thus containing four additional nitrogen atoms compared to the TAPP system. We also focused on the characterization of the corresponding reduced compounds, including the isolation of the radical anion, to gain further insights into its electronic behavior and stability of this new class of organic functional dyes.

Results and Discussion

At the beginning of this study we performed a computational screening of a range of different azaperopyrenes derived from the TAPP reference system[58] by successive [CH→N] replacement. This was meant to assess the effect of such modifications within the “structural space” of the peropyrene core and to assess potential synthetic N-atom rich target compounds gauged on the basis of their potential properties and stability.

Computational modeling of the frontier orbital energies of n-azaperopyrenes (n = 4–8)

A useful approach for a computational screening of the electron acceptor properties of polycyclic aromatic compounds is based on readily calculated LUMO energies. For the non-substituted tetraazaperopyrene TAPP the LUMO energy was previously determined to be significantly higher than the work function of gold,[38,42–43] which is widely used as the standard testing electrode for organic transistors.[10] Further decrease of the LUMO energy of TAPP was based on isosteric replacement of CH-units with nitrogen atoms in the peropyrene core, and to this end we modeled the frontier orbital energies screening a set of polyazaperopyrenes by means of DFT at the B3LYP/Def2-TZVPP-GD3(BJ)[60–66] level of theory (see Supporting Information for details). As validated in previous studies on tetraazaperopyrenes,[38,43–45] the chosen functional/basis set combination is suitable for a direct comparison of the DFT-LUMO energies with the work function of gold and generally gives rise to a good agreement between calculated and experimentally derived frontier orbital energy dependent properties (see below).

The comparison of the known tetraazaperopyrene derivatives with an electron withdrawing perfluoroalkyl group (CF$_3$) and an electron donating alkyl group (CH$_3$) at the 2- and 9-positions revealed a difference of ~0.6 eV of the LUMO energy.[38,43] Since both series of derivatives were assumed to be equally accessible, the energetically more stabilized 2,9-Bis(trifluoromethyl)-1,3,8,10-tetraaza-peropyrene (CF$_3$-TAPP) was chosen as reference system for a computational screening, with up to four additional nitrogen atoms to be incorporated in the polycyclic aromatic core. Since perylene cores with vicinal nitrogen substitution are known to be challenging to synthesize,[57] only those peropyrenes without vicinal nitrogen atoms were considered (for the full screening, see below and Supporting Information).

Beginning with the known TAPP reference system,[38,43] the expected trend towards lower frontier orbital energies was found upon increasing the number of nitrogen atoms in ortho and bay position, with the latter having a smaller effect (Figure 1). This can be explained by the larger orbital coefficients of the frontier orbitals in the ortho position of the TAPP, as well as slightly higher Mulliken charges at this position (see Supporting Information, Figure S1). Generally, we found a linear correlation between the number of [CH→N] replacements and the frontier orbital energies which were modeled only for the cases of purely bay or ortho N-substituted derivatives while mixed patterns were not considered at first. This observed linearity is due to the shape of the frontier orbitals being nearly independent of the specific aza substitution and reflected in the different bay and ortho N-substituted constitutional isomers of hexaazaperopyrene delivering nearly the same frontier orbital energies.

Notably, the HOMO-LUMO gap (ΔSCF) was slightly reduced with increasing nitrogen substitution in the bay positions. Therefore, an ortho [CH→N] replacement appeared more attractive in an initial synthetic approach as a larger HOMO-

![Previous work:](image1.png)

![This work:](image2.png)

Scheme 1. Previously synthesized ortho and bay substituted TAPPs (left) and the approach to synthesize an OAPP (right).
LUMO energy gap was thought to lead to more stable electron acceptor materials.\[68–70\] We therefore chose the planar, ortho azasubstituted octaazaperopyrene (OAPP), representing the extreme, as first synthetic target in this context.

Synthesis of octaazaperopyrene

As the starting material for the synthesis of octaazaperopyrenes (OAPP) we employed the inexpensive 1,3-acetonedicarboxylic acid diethyl ester. The naphthyridine structure is generated by a Knoevenagel reaction followed by an intramolecular cyclization (Scheme 2).\[71\] Campbell et al. observed that compound 2 dimerized under ambient aerobic conditions and that this reaction could be accelerated by adding $\text{H}_2\text{O}_2$ to obtain the 

The octachloro tetraazaperylene 4 was found to be highly reactive towards nucleophiles, and the nucleophilic attack of primary amines or alcohols to take place in the peri-position selectively.\[74\] 4-Methoxybenzylamine was used to introduce the amino function in the peri position giving compound 5, which was subsequently deprotected by refluxing in TFA according to a similar literature procedure.\[75\] Finally, the tetraamine 6 reacted with acyl chlorides under the standard reaction conditions previously established for the TAPP synthesis to form the octaazaperopyrene structure.\[72–73\] The almost insoluble blue compound 3 could be activated for further transformation by converting the hydroxy groups to chlorosubstituents, as first described in 1991 by Höchstetter.\[74\]

The electron density of the azaperopyrene core was increased by a palladium catalyzed dehalogenation\[76\] of the bay chlorinated...
derivatives 7a–f, which resulted in a planarization of the perylene core. Similar to 7, compounds 8a–f were isolated in their reduced (formally hydrogenated) state. All of the compounds 8a–f were only sparingly soluble in common solvents which is to be viewed as resulting from the planarization of the polycyclic aromatic cores and the capability to form intermolecular H-bonds.

Finally, compound 8c was oxidized with MnO₂ to give the target OAPP 9c (Scheme 3). To avoid decomposition, the oxidation was carried out under argon atmosphere. The OAPP is not stable at r.t. and can be handled only for a few minutes under argon atmosphere. Only compound 9c was isolated as a pure compound due to the thermal instability of the OAPPs in their oxidized form. For all the other derivatives, unspecific decomposition was observed during the oxidation.

Crystal structures

Single crystal X-ray structure analyses of the twisted dihydro-OAPP 7a and the protonated, unsubstituted dihydro-OAPPs 8a and 8e were obtained from hot concentrated solutions in ethanol (7a), sulfuric acid (8a) and HCl_{aq} (8e). The structural data of 7a confirm that the compound is in the reduced state. The NH proton forms a hydrogen bond (1.81 Å) with an ethanol molecule. As a bay chlorinated derivative 7a displays a significant twist of 33.7° (θ) between the tetraazaphenalenyl subunits of the peropyrene core which results from steric pressure of the four chlorine substituents (Figure 3). This observed twist is comparable to that of the bay chlorinated TAPP (29.4°–32.4°) as well as structurally similar PDIs.[46,77] The C–C bonds between the two tetraazaphenalenyl units have a length of 1.47 Å which is longer than for the phenalenyl units of the corresponding bay chlorinated TAPP (1.42 Å) and longer than typical aromatic C–C bonds.[46] This suggests incomplete delocalization of the π-electrons over the peropyrene core. The individual tetraazaphenalenyl units are also strained because of the twist, resulting in the increased bond length between C10 and C17 (1.45 Å) compared the other aromatic C–C bonds (1.38–1.40 Å). The packing pattern in the solid state shows an intermolecular π–π-stacking of two adjacent tetraazaphenalenyl units with a plane distance of 3.5 Å, leading to a slipped-stack packing pattern (Figure 3c).

The crystal structure of the dehalogenated, protonated OAPP [H₂8a]²⁺ was determined and revealed that this compound also was in the reduced dihydro state. The acidic medium (H₂SO₄) was employed for crystal growth because the planarized molecular compound resulting from the hydrodechlorination step proved to be only sparingly soluble in common organic solvents. Consequently, this OAPP derivative 8a is twice protonated in the isolated hydrogensulfate salt. Analogous to compound 7a, which was hydrogen bonded to a solvent molecule, the proton of the NH group forms a hydrogen bond with the hydrogensulfate counterion (distance: 2.14 Å). As confirmed in the X-ray diffraction study, the dehalogenation has led to a planarization of the peropyrene core (Figure 4b), which is rendered similar to the unsubstituted TAPP.[38]
planarization results in a reduction of steric stress in the naphthyridine core and consequently the bond length between C10 and C17 decreases to 1.42 Å. The other bond lengths are nearly identical compared to compound 7a, for instance, the C–C bond length between the two tetraazaphenalenyl units remains at 1.47 Å. OAPP 8a packs in a zigzag packing pattern with a π-π distance of 5.96 Å. The large π-π distance results from an alternating sequence of an OAPP layer and a hydrogen sulfate layer in the solid state structure (Figure 4c).

Apart from these two perfluoralkylated derivatives, single crystals were obtained for the protonated 1,9-dipropyl derivative [H₈Ba]⁺⁺ (Figure 5a) from an aqueous solution of HCl. Although alkylation increases the electron density compared to the perfluoroalkylated derivatives and would thus destabilize the reduced state, the solid state structure of compound 8e also confirmed the dihydro form in this case. The C–C bond length for the C10-C17-bond is again 1.47 Å and, as with also confirmed the dihydro form in this case. The C

The UV/Vis spectra and emission spectra of the R-OAPP-Cl (7a–f in THF), R-OAPP–H (8a–8f in TFA) and 9c, (in THF) are displayed in Figure 6. Similar to the TAPP derivatives, the absorption maxima are nearly constant within the respective series of 1,9-bisperfluoroalkyl or 1,9-dialkyl derivatives. Overall, the perfluorination of the alkyl chains results in a shift of the absorption maxima of 35 nm. The derivatives 8 were measured in trifluoroacetic acid due to their low solubility. The absorption maxima were at 385 nm for the alkylated and at 414 nm for the perfluoroalkylated derivatives. In contrast to the twisted OAPP (7), the maxima of the alkylated compounds have a smaller wavelength than the perfluoroalkylated ones. Only the alkylated derivatives displayed emission in solution and the fluorescence spectra are also shown in Figure 6a,b (dashed lines). The absorption and emission spectra of the “oxidized” form of 8c, the target OAPP compound (9c) was recorded in THF due to its

![Figure 4](image_url) Solid state structure of [H₈Ba]⁺⁺ crystallized in sulfuric acid from top view (a) and side view (b); the compound exhibits a zigzag packing pattern with alternating layers of [H₈Ba]⁺⁺ and hydrogen sulfate (c).

![Figure 5](image_url) Solid-state structure of [H₈Be]⁺⁺ crystallized in hydrochloric acid from top view (a) and side view (b); the packing pattern delivered a slipped-stack packing pattern (c) (the solvent molecules are omitted for clarity).

| Crystal system | Space group  | π-π Plane distance [Å] | Torsion Angle θ [°] |
|----------------|-------------|------------------------|---------------------|
| 7a⁺⁺ | triclinic P-1 | 3.517 | 33.7(4) |
| [H₈Ba]⁺⁺⁻ | monoclinic P2₁/c | 5.956 | 42.2(13) |
| [H₈Be]⁺⁺ | triclinic P-1 | 3.380 | 1.4(3) |

(a) π-π plane distance was measured between two adjacent tetraazaphenalenyl subunits. (b) Torsion angle was measured between both tetraazaphenalenyl subunits of one molecule. (c) 7a co-crystallized with ethanol. (d) [H₈Ba]⁺⁺ crystallized as hydrogen sulfate. (e) [H₈Be]⁺⁺ crystallized as chloride.
greater solubility in such an organic solvent as compared to the hydrogen bonded reduced dihydro form. It displayed an absorption maximum at 400 nm and in contrast to the derivatives 7 and 8, a strongly Stokes shifted emission spectrum (Figure 6c). The optical properties of compounds 7–9 are summarized in Table 2.

Table 2. Photophysical properties of 7, 8, and 9.

| Compound | λ_{abs} [nm] | λ_{em} [nm] | 0-0-Transition [nm] | Stokes shift [cm\(^{-1}\)] |
|----------|---------------|-------------|---------------------|--------------------------|
| 7a       | 449 (4.24)    | /           | /                   | /                        |
| 7b       | 447 (4.27)    | /           | /                   | /                        |
| 7c       | 447 (4.28)    | /           | /                   | /                        |
| 7d       | 483 (4.23)    | 550         | 526                 | 2522                     |
| 7e       | 484 (4.29)    | 555         | 531                 | 2643                     |
| 7f       | 484 (4.34)    | 558         | 532                 | 2740                     |
| 8a       | 414 (4.51)    | /           | /                   | /                        |
| 8b       | 415 (4.54)    | /           | /                   | /                        |
| 8c       | 415 (4.53)    | /           | /                   | /                        |
| 8d       | 386 (4.18)    | 582         | 509                 | 8725                     |
| 8e       | 386 (4.29)    | 581         | 505                 | 8695                     |
| 8f       | 386 (4.22)    | 581         | 502                 | 8695                     |
| 9c       | 400 (4.45)    | 561         | 477                 | 7175                     |

Redox properties of the OAPP derivative 9c

The redox properties of the only OAPP-derivative, which was isolable in its TAPP-analogous “oxidized” form, compound 9c were investigated by cyclic voltammetry. Two separate one electron reduction steps were found in the cyclic voltammogram (see Figure 7). The first reduction step was found to be fully reversible, leading to the monoanionic radical species. The second reduction step exhibited quasi-reversible electron transfer characteristics and gave rise to the di-anionic OAPP. Complete decomposition of the material was observed after eight cycles, indicating the reactivity and thus lability of the OAPP redox states involved.

According to a method, which is widely employed in the literature the energy of the LUMO was estimated from the measured potential of the first reduction wave via subtraction of the potential of ferrocene (4.8 eV Fc/Fc\(^{+}\)) as reference system.\(^{[79]}\) In comparison to the corresponding TAPP (LUMO: −3.72 eV) the LUMO energy is decreased by 0.7 eV due to the isosteric replacement of a further four CH-units with nitrogen.

To gain deeper insight into the electronic properties of compound 9c, and thus generally OAPPs, various band gap-related energies of the synthetically accessible OAPP 9c were
modeled by DFT and TD-DFT. The validity of the results at the chosen level of theory (UB3LYP/Def2-TZVPP-GD3(BJ) with and without CPCM[48–51] as solvation model, see Supporting Information for details) could be gauged by direct comparison of the computed LUMO and optical band gap energies (\(E_{\text{opt}}\)) with the estimates based on experimental redox and photophysical data (see below). Singlet excitation energies were obtained as vertical excitations using TD-DFT, while the fundamental band gap energy \(E_F\) (or transport energy gap) was derived employing the delta self-consistent field approach (\(\Delta E_{\text{SCF}}\)) [80–81]. With the latter, the fundamental band gap \(E_F\) could be determined from the SCF orbital energies and the resulting SCF total energies for the neutral, oxidized, or reduced systems separately and then inserting them into the relation:

\[
\Delta E_F = I_{\text{opt}} - A_{\text{opt}} = [E_{\text{opt}} - E_{\text{opt}}]\]

Herein, \(I_{\text{opt}}\) and \(A_{\text{opt}}\) refer to the ionization potential and the electron affinity of the neutral compound, respectively, and \(E_{\text{opt}}\) is the total SCF energy of the oxidized, neutral, or reduced compound. The calculated fundamental gap energies were determined to be \(\Delta E_{\text{opt}} = 5.42\) eV in the gas phase and \(\Delta E_{\text{opt}} = 3.17\) eV in solution. The energies of the frontier orbitals and the highest occupied molecular orbital with \(\pi\)-character (HOMO) were extracted directly from the single point calculations of the neutral compound as SCF-orbital energies. Here, an excellent agreement of the theoretical and experimental determined energetic LUMO position can be seen (see Table 3). A remarkably good agreement with the experiment is also noticeable when considering the calculated optical band gap \(E_{\text{opt}}\). Using TD-DFT, this was determined to be the first most intense singlet transition \(S_0 \rightarrow S_1\), mixing of HOMO-2 \(\rightarrow\) LUMO + 1, HOMO-1 \(\rightarrow\) LUMO, and HOMO \(\rightarrow\) LUMO). Three other weakly or non-dipole allowed singlet excitations are hidden under the absorption band of the \(S_0 \rightarrow S_1\) excitation (for TD-DFT spectrum, see Supporting Information).

The radical anion of \(9\text{c OAPP}^+\) was isolated in nearly quantitative yield by addition of one equivalent of KC\(_8\) to a suspension of OAPP \(9\text{c}\) in THF [48]. The radical anion was characterized by EPR spectroscopy and revealed a g-factor of 2.003 (Figure 8), which is in accordance with typical delocalized organic radicals. Hyperfine coupling to \(^{14}\text{N}\) \((I = 1)\) was not resolved for this system [48].

Discussion of the isosteric replacement [CH \(\rightarrow\) N] in azaperopyrenes and general conclusions related to this family of poly-N-heterocyclic aromatic compounds

In this study, we extended the chemistry of azaperopyrenes (APPs), taking the previously studied TAPP as reference system, by isosteric replacement of four additional \(\text{CH}\)-units with nitrogen. In order to generalize the insights into the influence of the number and the position of the aza substitution we conclude this study by extending the computational screening to include all conceivable and distinct permutations of the isosteric [CH \(\rightarrow\) N] replacement at the ortho and bay positions of the CF\(_3\)-TAPP.

Generally and notably, we found a 2D linear correlation between the number of the nitrogen atoms in the aromatic core, the position of the nitrogen atoms and the HOMO and LUMO energies (Figure 9a). The ortho and bay [CH \(\rightarrow\) N] replacements independently decrease the frontier orbital energies by a defined value, more precisely each ortho aza substitution results in a decrease of 0.31 eV for the HOMO and 0.26 eV for the LUMO and for a bay substitution a reduction of 0.15 eV for the HOMO and 0.17 eV for the LUMO energy was identified (see Equation I and II). That the ortho isosteric replacement leads to a higher decrease of the frontier orbital energies can be traced to the larger orbital coefficients in this position (see above).

\[
E_{\text{HOMO}} = (-6.80 - 0.310 - 0.15b) \text{ eV} \tag{1}
\]
\[
E_{\text{LUMO}} = (-3.82 - 0.260 - 0.17b) \text{ eV} \tag{2}
\]

Table 3. Electronic properties of \(9\text{c}\) OAPP\(^+\) according to DFT calculations and CV and UV/Vis experiments.

| Solvent model | \(E_{\text{HOMO}}\) [eV] | \(E_{\text{LUMO}}\) [eV] | \(E_{\text{SCF}}\) [eV] | \(E_{\text{HOMO}}\) [eV] | \(E_{\text{LUMO}}\) [eV] | \(E_{\text{opt}}\) [eV] |
|---------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Gas           | 3.76           | -8.01          | -8.23          | -4.90          | 5.42           | 3.17           |
| thf           | 4.54           | -7.74          | -7.80          | -4.44          | 3.17           | 3.11           |

\[\Delta E_{\text{opt}}\] Properties were calculated using the \(\Delta \text{SCF}/\text{DFT}\) approach. Properties were calculated as the SCF-orbital energies of the neutral compound. The optical band gap \(E_{\text{opt}}\) was obtained as the first singlet state with the largest oscillator strength via TD-DFT. Values were determined experimentally. HOMO: highest occupied molecular orbital with \(\pi\)-character; \(E_{\text{opt}}\): fundamental band gap; \(E_{\text{opt}}\): optical band gap.
(a = number of nitrogen in the ortho position, b = number of nitrogen in the bay position)

For constitutional isomers with a vicinal N–N arrangement, the HOMO energies deviate from the idealized Equation I, and are higher than expected (Figure 9b). This result arises from the fact that in these isomers the HOMO has $\sigma$-symmetry within the aromatic plane and significant lone pair character, mainly localized at the vicinal nitrogen atoms (Figure 10b). Therefore, the resulting Pauli repulsion of the N-lone pairs increases the energy of this type of HOMO. However, if one considers the highest occupied molecular orbital with $\pi$-character (HOPMO) for these constitutional isomers, instead of the lone pair based HOMOs, a good agreement (Figure 9b) with the linearly approximated HOMO energies in Equation I is generally found. Notably, for the case of two pairs of vicinal nitrogen atoms in one molecule, the HOPMO was in accordance to the expected HOMO energies for the derivatives with two bay and two orthoaza substitutions. On the other hand, for higher numbers of nitrogen atoms (e.g., four ortho + two bay) the HOPMO energies are lower than expected. Generally the deviation of the LUMO energies of the vicinally substituted isomers compared to the other isomers is small and insignificant given the DFT method employed.

In summary, the peropyrene structure allows the specific variation of the frontier orbital energies for a certain application by adding nitrogen atoms into the aromatic core. This in principle allows the tuning of the LUMO energy close to the work function of gold, which is important for the use of the azaperopyrenes as $n$-semiconducting materials, without adding substituents to the aromatic core. In the development of nitrogen rich N-heteropolycycles based on the peropyrene core structure the OAPP reported and characterized in this work represents an extreme case as electron acceptors. In terms of [CH–N] replacements current and future work in our lab will therefore address the chemical space between the TAPPs and the OAPPS.

**Experimental Section**

**General Information**

All chemicals and solvents were purchased from commercial suppliers and used without further purification. Solvents were dried according to standard procedures. Deuterated solvents were bought from Euriso Top or Sigma Aldrich and used as received. The $^1$H, $^{13}$C and $^{19}$F spectra were recorded with Bruker AVANCE 400 and 600II spectrometers and are referenced to the residual signal of the used deuterated solvents ($^1$H: CDCl$_3$: 7.26 ppm, THF-d$_8$: 1.72 ppm/3.58 ppm, DMSO-d$_6$: 2.50 ppm) and $^{13}$C: CDCl$_3$: 77.16 ppm, THF-d$_8$: 67.21 ppm/25.31 ppm, DMSO-d$_6$: 39.52 ppm.$^{[84]}$ Chemical shifts are given in ppm and coupling constants in Hz. The following abbreviations were used to describe the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet. The mass spectra were recorded by the department of the organic Chemistry of the University of Heidelberg under the direction of Dr. J. Gross. EI spectra were measured on a JEOL JMS 700 spectrometer, ESI spectra on a Bruker ApexQe hybrid 9.4 T FT-ICR (also for MALDI spectra) or a Finnigan LCQ spectrometer. The absorption spectra were recorded on a Cary 5000 UV/Vis- spectrometer and were baseline and solvent corrected. The Fluorescence spectra were recorded on a Varian Cary Eclipse Fluorescence spectrophotometer.
The Fluorescence Yields (Φ) were conducted on a JASCO spectrofluorometer FP-8500 equipped with an ILF-835 100 mm integrating sphere. Cyclic voltammetry spectra were measured on an EG&G Princeton Applied Research Research potentiostat model 263 A using a three-electrode single-component cell under inert atmosphere. A platinum disk was used as working electrode, platinum wire as a counter electrode and a saturated calomel electrode as a reference electrode. As internal reference ferrocene was used in all cases. Measurements were carried out in a 0.1 M tetrabutylammonium hexafluorophosphate solution in anhydrous THF and exclusion of oxygen. X-ray analyses were performed by Prof. Dr. H. Wadepohl in the structure-analytical laboratory of the Department of Inorganic Chemistry at the University of Heidelberg with a Bruker AXS Smart 1000 diffractometer or an Agilent Supernova E diffractometer. The obtained structures were resolved by Prof. Dr. H. Wadepohl.

Infrared spectra were measured on a Bruker FT IR with a Germanium ATR crystal. Unless otherwise stated, all preparative work was performed in an inert gas atmosphere in standard Schlenk glassware, which was flame-dried.

**General Procedure 1**

3,4,9,10-tetraamino-1,6,7,12-tetrachloro-2,5,8,11-tetraazaperylene (1.00 eq.) was dissolved in 1,4-dioxane. Triethylamine (3.00 eq.) and acetyl chloride (5.50 eq.) were added and the reaction solution was stirred at 100 °C for 7 d. The reaction mixture was allowed to cool down to r.t. and the resulting precipitate was filtered. The residue was washed with water and the crude product was recrystallized from ethanol to yield the product as an orange solid.

**General Procedure 2**

Formic acid (36.0 eq.) was dissolved in DMF, triethylamine (36.0 eq.) and acetone (36.0 eq.) were added and the resulting precipitate was stirred at 100 °C for 2 d. The reaction mixture was allowed to cool down to r.t. and poured onto water. The resulting precipitate was filtered and washed with H₂O, acetone and THF.

**2,7-Naphthylidine-1,3,6,8-tetraol (2)**

Diethyl-1,3-acetonedicarboxylate (35.9 ml, 198 mmol, 1.00 equiv.) was dissolved in 350 ml ethanol, malononitrile (15.7 g, 237 mmol, 1.20 equiv.) and diethyl amine (2.7 ml, 26 mmol, 0.13 equiv.) were added and the reaction mixture was stirred at r.t. for 2d. The solvent was removed under reduced pressure and the product was obtained as a red orange solid (13.5 g, 14.4 mmol, 77%).¹³C NMR (600.13 MHz, CDCl₃, 295 K): δ [ppm] = 169.6, 169.3, 165.6, 163.6, 162.5, 151.3, 148.8, 104.7, 89.1, 35.7. HRMS (MALDI): calcd. for C₁₄H₁₂N₂O₂ (M⁺): 206.0840; found: 206.0841. Analytics are in agreement with previously reported data.³⁷¹

**4,10-Dihydroxy-5,11-dihydro-2,5,8,11-tetraazaperylenyl-e1,3,6,7,9,12-hexaone (3)**

1,3,6,8-tetrahydroxy-2,7-naphthylidine (10.0 g, 51.5 mmol, 1.00 equiv.) was suspended in 210 ml 0.25 M NaOH solution and H₂O₂ (6.4 ml, 206 mmol, 4.00 eq.) was added over a period of 4 h. The reaction mixture was stirred for 16 h at room temperature and the resulting precipitate was filtered. The residue was washed with 1.0 H₂O to yield 3 as a blue solid (8.11 g, 21.2 mmol, 82%).¹³C NMR (150.90 MHz, D₂SO₄, 295 K): δ [ppm] = 167.3, 162.3, 136.8, 124.8, 88.4. HRMS (ESI⁺): calcd. for C₁₅H₁₄N₂O₂ (M–H⁺): 381.01129; found: 381.0091. Analytics are in agreement with previously reported data.³⁷²

**1,3,4,6,7,9,10,12-Octachloro-2,5,8,11-tetraazaperylene (4)**

4,10-dihydroxy-5,11-dihydro-2,5,8,11-tetraazaperylene, 1,3,6,7,9,12-hexaone (2.50 g, 6.54 mmol, 1.00 equiv.) and PCl₅ (25.0 g, 120 mmol, 18.4 equiv.) were dissolved in POCl₃ (25 ml, 268 mmol, 41.0 equiv.). The reaction mixture was stirred at 160 °C for 2 d. The reaction mixture was poured on ice and the resulting precipitate was filtered. The residue was washed with 500 ml H₂O to yield 4 as an orange solid (2.10 g, 3.95 mmol, 83%).¹³C NMR (150.90 MHz, nitrobenzene-d₄, 295 K): δ [ppm] = 148.3, 146.5, 144.6, 117.1, 116.9. HRMS (MALDI⁺): calcd. for C₁₄H₆Cl₄N₂ (M⁺): 527.7637; found: 527.7642.

**1,6,7,12-Tetrachloro-N,N,N',N'-tetakis(4-methoxybenzyl)dipyrido[3,4,5-de:3',4',5'-gh][2,9]phenanthroline-3,4,9,10-tetraamine (5)**

1,3,4,6,7,9,10-octachloro-2,5,8,11-tetraazaperylene (10.0 g, 18.8 mmol, 1.00 equiv.) was dissolved in 150 ml o-xylene. 4-methoxy benzylamine (61.0 ml, 470 mmol, 25.0 eq.) was added and the reaction mixture was stirred at 150 °C for 3 h. The solution was allowed to cool to r.t. and poured onto 400 ml methanol. The resulting precipitate was filtered, washed with 400 ml H₂O and 400 ml methanol. Solvent residuals were removed under reduced pressure and the product was obtained as a red orange solid (13.5 g, 14.4 mmol, 77%).¹³C NMR (600.13 MHz, CDCl₃, 295 K): δ [ppm] = 7.14 (d, J=E=7.95 Hz, 8H), 6.81 (d, J=E=8.30 Hz, 8H), 5.79 (s, 4H, NH), 4.50-4.43 (m, 8H), 3.81 (s, 12H).¹³C NMR (150.90 MHz, CDCl₃, 295 K): δ [ppm] = 159.2, 152.6, 144.6, 144.0, 129.7, 129.4, 125.8, 114.2, 98.5, 55.3, 46.4. HRMS (MALDI⁺): calcd. for C₂₉H₁₆Cl₂N₄O₄ (M⁺): 592.1921; found: 592.1941.

**3,4,9,10-Tetraamino-1,6,7,12-tetrachloro-2,5,8,11-tetraazaperylene (6)**

Compound 5 (13.5 g, 144 mmol, 1.00 equiv.) was dissolved in 100 ml TFA and stirred at 80 °C for 16 h. The solution was allowed to cool to r.t. and the solvent was removed under reduced pressure. The resulting precipitate was filtered, washed with 400 ml H₂O and 400 ml methanol. Solvent residuals were removed under reduced pressure and the product was obtained as a red orange solid (13.5 g, 14.4 mmol, 77%).¹³C NMR (600.13 MHz, DMSO-d₆, 295 K): δ [ppm] = 7.25 (s, 8H).¹³C NMR (150.90 MHz, DMSO-d₆, 295 K): δ [ppm] = 154.5, 145.5, 144.8, 107.7, 96.8. HRMS (MALDI⁺): calcd. for C₂₆H₁₂Cl₂N₄O₂ (M⁺): 451.9621; found: 451.9625.

**Compound 7a**

According to GP 1 3,4,9,10-tetraamino-1,6,7,12-tetrachloro-2,5,8,11-tetraazaperylene (750 mg, 1.65 mmol, 1.00 eq.) was dissolved in 20 ml 1,4-dioxane. Triethylamine (690 µl, 4.95 mmol 3.00 eq.) and TFAA (1.26 ml, 9.08 mmol, 5.50 eq.) were added and the reaction solution was stirred at 60 °C for 7 d. The reaction mixture was allowed to cool down to r.t. and the resulting precipitate was filtered. The residue was washed with water and the crude product

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According to GP1 3,4,9,10-tetraamino-1,6,7,12-tetrachloro-2,5,8,11-tetraazaperylene (750 mg, 1.65 mmol, 1.00 eq.) was dissolved in 20 ml 1,4-dioxane. Triethylamine (690 μl, 4.95 mmol 3.00 eq.) and pentafluoropropionic anhydride (1.79 ml, 9.08 mmol, 5.50 eq.) were added and the reaction solution was stirred at 100°C for 7 d. The reaction mixture was allowed to cool down to r.t. and the resulting precipitate was filtered. The residue was washed with water (2x 50 ml) and the crude product was recrystallized from ethanol to yield the product as an orange solid (552 mg, 872 μmol, 85 %). HRMS (MALDI−): calcd. for C_{53}Cl_{14}F_{23}N_{8} (M−) (oxidized form): 605.8910; found: 605.8910.

Compound 7b

According to GP1 3,4,9,10-tetraamino-1,6,7,12-tetrachloro-2,5,8,11-tetraazaperylene (750 mg, 1.65 mmol, 1.00 eq.) was dissolved in 20 ml 1,4-dioxane. Triethylamine (690 μl, 4.95 mmol 3.00 eq.) and pentafluoropropionic anhydride (1.79 ml, 9.08 mmol, 5.50 eq.) were added and the reaction solution was stirred at 100°C for 7 d. The reaction mixture was allowed to cool down to r.t. and the resulting precipitate was filtered. The residue was washed with water (2x 50 ml) and the crude product was recrystallized from ethanol to yield the product as an orange solid (906 mg, 1.12 mmol, 51 %). HRMS (MALDI−): calcd. for C_{53}Cl_{14}F_{23}N_{8} (M−) (oxidized form): 605.8910; found: 605.8910.

Compound 7c

According to GP1 3,4,9,10-tetraamino-1,6,7,12-tetrachloro-2,5,8,11-tetraazaperylene (1.00 g, 2.20 mmol, 1.00 eq.) was dissolved in 30 ml 1,4-dioxane. Triethylamine (920 μl, 6.61 mmol 3.00 eq.) and perfluorobutyryl chloride (1.80 ml, 12.1 mmol, 5.50 eq.) were added and the reaction solution was stirred at 100°C for 7 d. The reaction mixture was allowed to cool down to r.t. and the resulting precipitate was filtered. The residue was washed with water (2x 50 ml) and the crude product was recrystallized from ethanol to yield the product as an orange solid (906 mg, 1.12 mmol, 51 %). HRMS (MALDI−): calcd. for C_{53}Cl_{14}F_{23}N_{8} (M−) (oxidized form): 605.8910; found: 605.8910.

Compound 7d

According to GP1 3,4,9,10-tetraamino-1,6,7,12-tetrachloro-2,5,8,11-tetraazaperylene (300 mg, 661 μmol, 1.00 eq.) was dissolved in 10 ml 1,4-dioxane. Triethylamine (275 μl, 1.98 mmol 3.00 eq.) and acetyl chloride (260 μl, 3.36 mmol, 5.50 eq.) were added and the reaction solution was stirred at 100°C for 7 d. The reaction mixture was allowed to cool down to r.t. and the resulting precipitate was filtered. The residue was washed with water (2x 50 ml), methanol (2x 20 ml) and the crude product was recrystallized from ethanol to yield the product as an orange red solid (183 mg, 364 μmol, 55 %). HRMS (MALDI−): calcd. for C_{53}Cl_{14}F_{23}N_{8} (M−) (oxidized form): 605.8910; found: 605.8910.

Compound 7e

According to GP1 3,4,9,10-tetraamino-1,6,7,12-tetrachloro-2,5,8,11-tetraazaperylene (750 mg, 1.65 mmol, 1.00 eq.) was dissolved in 15 ml 1,4-dioxane. Triethylamine (690 μl, 4.95 mmol 3.00 eq.) and butyryl chloride (940 μl, 9.08 mmol, 5.50 eq.) were added and the reaction solution was stirred at 100°C for 7 d. The reaction mixture was allowed to cool down to r.t. and the resulting precipitate was filtered. The residue was washed with water (2x 50 ml) and the crude product was recrystallized from ethanol to yield the product as an orange solid (556 mg, 996 μmol, 60 %). HRMS (MALDI−): calcd. for C_{53}Cl_{14}F_{23}N_{8} (M−) (oxidized form): 572.0482; found: 572.0482.
Compounds 8c
According to GP2 formic acid (838 μl, 22.2 mmol, 36.0 eq.) was dissolved in 15 ml DMF, triethylamine (3.10 ml, 22.2 mmol, 36.0 eq.) was added dropwise and stirred at r.t. for 30 min. [Pd(PPh3)4] (143 mg, 123 μmol, 20 mol%), compound 7c (500 mg, 617 μmol, 1.00 eq.) were added and the reaction mixture was stirred at 80°C for 2 d. The reaction mixture was allowed to cool down to r.t. and poured onto 150 ml water. The resulting precipitate was filtered and washed with H2O (3x 50 ml), acetone (2x 30 ml) and THF (2x 30 ml) to yield the product as an orange red solid (328 mg, 14.55, 138.4 (q, JF-F = 13.2 Hz), 120.2, 113.7.1°C signals of the N-C-N- and perfluorinated alkyl groups could not be detected due to coupling to fluorine groups.²F NMR (379.27 MHz, D2O-d4, 295 K): δ [ppm] = -80.1 (t, 2JF-F = 8.87 Hz, 6F), -117.2 (s, 4F), -124.8 (s, 4F), HRMS (MALDI⁺): calcd. for C32H31F14N8 (M⁺) (oxidized form): 670.0341; found: 670.0342.

Compounds 8d
According to GP2 formic acid (1.11 ml, 29.3 mmol, 36.0 eq.) was dissolved in 15 ml DMF, triethylamine (4.09 ml, 29.3 mmol, 36.0 eq.) was added dropwise and stirred at r.t. for 30 min. [Pd(PPh3)4] (188 mg, 163 μmol, 20 mol%), compound 7d (409 mg, 815 μmol, 1.00 eq.) were added and the reaction mixture was stirred at 80°C for 2 d. The reaction mixture was allowed to cool down to r.t. and poured onto 150 ml water. The resulting precipitate was filtered and washed with H2O (3x 50 ml), acetone (2x 30 ml) and THF (2x 30 ml) to yield the product as an orange red solid (101 mg, 277 μmol, 34%). 1H NMR (600.13 MHz, D2O-d4, 295 K): δ [ppm] = 8.43 (s, 4H), 2.58 (s, 6H), 13C NMR (150.90 MHz, D2O-d4, 295 K): δ [ppm] = 138.0, 148.3, 144.2, 137.2, 118.4, 111.1, HRMS (MALDI⁺): calcd. for C50H31F12N8 (M⁺): 812.1726; found: 812.1726.

Deposition Numbers
Deposition Number(s) 2130535 (for 4), 2130536 (for 7a), 2130537 (for 8a) and 2130538 (for 8e) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe “http://www.ccdc.cam.ac.uk/structures”Access Structures service.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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[1] J.-F. Morin, J. Mater. Chem. C 2017, 5, 12298–12307.
[2] A. Nowak-Kröll, F. Würtzenth, Org. Chem. Front. 2019, 6, 1272–1318.
[3] Q. Mao, Adv. Mater. 2014, 26, 5541–5549.
[4] U. H. F. Bunz, Acc. Chem. Res. 2015, 48, 1676–1686.
[5] U. H. F. Bunz, J. U. Engelhart, Chem. Eur. J. 2016, 22, 4680–4689.
[6] U. H. F. Bunz, J. Freundenberg, Acc. Chem. Res. 2019, 52, 1575–1587.
