Conjugated Materials

Twisting the TAPPs: Bay-Substituted Non-planar Tetraazaperopyrenes and their Reduced Anions

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Abstract: A new synthesis of tetraazaperopyrenes (TAPPs) starting from a halogenated perylene derivative 3,4,9,10-tetrabromo-6,7,12-tetrachloroperylene (1) gave access to bay-substituted TAPPs for the first time. Selective lithiation of the bromine-positions and subsequent addition of tosyl azide led to the formation of the tetraazidotetrachloroperylene (2), which was subsequently reduced by addition of sodium borohydride to the corresponding tetraaminotetrachloroperylene (3). Oxidation to its semiquinoidal form 4 and subsequent cyclization with acid chlorides gave rise to a series of bay-chlorinated TAPPs. Whereas the aromatic core of the previously studied ortho-substituted TAPPs was found to be planar, the steric pressure of the two chlorine substituents on each side leads to the twist of the peropyrene core of approximately 30 degrees, a structural feature also observed in other bay-substituted perylene derivatives. An experimental and computational analysis reveals that introducing chloride substituents at these positions leads to slightly increased electron affinities (EA) enabling the selective generation and characterization of the reduced mono-anionic radicals and closed shell di-anionic species. These anions were isolated and characterized by UV/Vis spectroscopy and EPR or NMR, respectively. Processing of the bay-chlorinated TAPPs in n-channel organic TFTs revealed electron mobilities of 0.001 to 0.003 cm²V⁻¹s⁻¹. These reduced electron mobilities compared to the ortho-halogenated TAPPs are thought to be rooted in the less densely packed solid-state structures.

Introduction

Perylene tetracarboxydiimides (PDIs) have been extensively studied as functional dyes and electronic materials.[1–17] Their properties may be varied widely by substitution at the perylene core and at the imido-N position. The carboxy substituents at the central perylene core render these materials electron acceptors, and this property in particular has been underlying their application in organic electronics.

Different synthetic approaches have been established to functionalize the bay,[2, 10–18] or ortho-[24–31] positions selective-ly or even to fully substitute[26, 32, 33] the perylene core in a single-step-reaction (Figure 1).[34, 35]

A class of molecular dyes which has displayed photophysical and redox properties similar to the ubiquitous PDIs are the tetraazaperopyrenes (TAPPs) which have been investigated for more than a decade.[36–48] Whereas the electron accepting character of the PDIs is due to carboximide substituents at both ends of the perylene core, TAPPs contain two pyrimidine rings fused with the central perylene unit. The electron accepting character of the resulting N-heteropolycycles is thus effectively built into the aromatic core itself rather than substituent-induced. Viewed alternatively, the fourfold isosteric [CH!N] substitution in the parent hydrocarbon peropyrene radically changes its electronic properties while leaving its molecular shape practically unchanged.

Figure 1. Left: Substituent positions in perylene derivatives. Right: bay- and ortho-substitution in PDIs.
 Whereas electrophilic substitution of PDIs and related compounds occurs in the bay-positions, the corresponding derivatization of the parent TAPP compounds (I) happened exclusively in the ortho-position, leaving the bay-CH units unaffected and thus maintaining the planar structure of the aromatic core (Scheme 1).\textsuperscript{42,48} Manifold derivatization of TAPP derivatives in the 2,9-positions, as well as in the ortho-position, has led to a detailed understanding of the molecular behavior and its photophysical and electronic properties. On the other hand, it has not yet been possible to functionalize the inner bay position of the peropyrene core, in order to establish a link with the well established PDI chemistry and its further development towards more complex polycyclic aromatics. Thus, a fundamental part of TAPP-chemistry has remained unexplored to date.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{scheme1.png}
\caption{Approach to synthesize ortho-substituted TAPP-derivatives (left, previous work) and inability to functionalize the bay-position (right) when starting from earlier parent compound I.}
\end{figure}

In this work, we report a novel TAPP synthesis, which for the first time allowed their bay functionalization. Additionally, a detailed study of their reduced species was conducted to gain insights into electronic behavior and their stability. Comparison of the ortho- and bay-chlorinated TAPPs provided insight into the influence of the different substitution patterns of the peropyrene core.

\section*{Results and Discussion}

\subsection*{Synthesis of bay-chlorinated TAPPs}

The starting material for the synthesis of bay-substituted TAPPs was tetrabromotetrachloroperylene (1), first published in 2014 (Scheme 2).\textsuperscript{49} Selective lithiation of the bromine positions and subsequent addition of tosyl azide led to the formation of the tetraazidotetrachloroperylene (2), which was subsequently reduced by addition of sodium borohydride to the corresponding tetraaminotetrachloroperylene (TAP-Cl, 3). Analogous to the previously reported non-chlorinated tetraaminoperylene, this compound displayed a tendency to be oxidized under ambient conditions to form the chlorinated dianinoperylenediimine (DPDI-Cl, 4), however, the reaction proceeded much more slowly than for the parent DPDI and occasionally did not go to completion. Therefore, oxidation to the semiquinoidal compound 4 was selectively carried out by the reaction of 3 with activated MnO\textsubscript{2}.

By employing the standard ring-closing reaction conditions of the original TAPP-synthesis, the first bay-substituted TAPP derivatives with H- or perfluoroalkyl-substituted 2- and 9-position (5) were obtained. As opposed to the planar ortho-substituted TAPP derivatives, which only possess low solubility in common organic solvents, the twist induced by the bay-chlorination leads to a significantly enhanced solubility.

\subsection*{Crystal structures of 5a–c}

Single crystals of the tetrachlorinated TAPPs 5a, 5b and 5c were grown by slow evaporation of concentrated solutions in chloroform (5a and 5c) and toluene (5b) (Figure 2). All three solid-state structures reveal a significant twist between the two diazaphenalenyl subunits of the tetraazaperopyrene core: 5a (29.4 degrees), 5b (30.6 degrees) and 5c (32.4 degrees). Whereas the aromatic core of the previously studied ortho-substituted TAPPs was found to be planar, the steric pressure of the two chlorine substituents on each side leads to the twist of the peropyrene core, a structural feature also observed in other bay-substituted perylene derivatives.\textsuperscript{18}

In all three cases, the packing pattern in the solid state is determined by intermolecular stacking of two diazaphenalenyl subunits. This motif leads to distances as close as 3.4 Å between the aromatic core halves of two adjacent molecules, however, the general packing pattern varies for the different perfluorinated alkyl chains (Figure 3). Thus, the CF\textsubscript{3}-substituted TAPP 5a packs in a zigzag fashion, while the elongation of the fluoroalkyl chains in 5b leads to more columnar-like packing pattern. The crystals of 5c could not be obtained without co-crystallization of solvent, which renders an assessment of the packing pattern less significant. The key data of the solid-state structures are summarized in Table 1.

\subsection*{Interconversion barrier of atropo-enantiomers}

As the steric repulsion between opposing chlorine atoms leads to the aforementioned torsion in the peropyrene backbone, the dye molecules possess helical chirality, leading to \textit{P-} and \textit{M-}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{scheme2.png}
\caption{Synthetic route to the bay-chlorinated DPDI analogue (DPDI-Cl, 4) and subsequent ring-closing reaction to the corresponding bay-TAPP-Cl 5.}
\end{figure}
M-atropoisomers (Scheme 3). This helical isomerism has been studied in detail for the structurally similar bay-functionalized perylene bisimides, and the interconversion barrier between the atropo-enantiomers was found to depend on the number and steric demand of the bay substituents. Whereas for most PDIs interconversion occurs rapidly at room temperature, larger substituents raise the energy barrier over 22.2 kcal mol$^{-1}$, which is the minimum barrier required for the isolation of the enantiomers at ambient temperature and the usual timescale of product handling. It was therefore of interest to compare analogously substituted PDI- and TAPP-systems in order to obtain insight into the flexibility of the peropyrene core compared to the PDI system.

To this end, the interconversion of the atropisomeric bay-chlorinated tetrazaperopyrenes, has been modeled theoretically by DFT (Scheme 4). For a potential one-step mechanism involving a planar transition state the energy barrier would be approximately 72 kcal mol$^{-1}$, thus locking the molecules in a single helical form. As an alternative pathway, the stepwise isomerization was investigated, in which the first transition state is reached via the planarization on only one side of the TAPP, while the opposite side remains in the twisted form. This results in a reduced torsion angle of about 10 degrees compared to 32 degrees in the ground state (Table 2). The computed activation energy was found to be 23.7 kcal mol$^{-1}$, and the resulting intermediate bay-substituted TAPP is characterized by mutually syn-oriented chloro substituents. This achiral intermediate is only 9 kcal mol$^{-1}$ higher in energy than the trans-oriented conformer and either reacts back to the initial form or to the other atropisomer.

**Table 1. Structural parameters of solid-state structures of 5a–c.**

| Crystal system   | Space group | π–π Plane distance [Å]$^{[a]}$ | Torsion angle [°]$^{[b]}$ |
|------------------|-------------|-------------------------------|--------------------------|
| 5a               | orthorhombic| 3.440                         | 29.43 (0.03)              |
| 5b               | monoclinic  | 3.535                         | 30.10 (0.03)              |
| 5c               | triclinic   | 3.603$^{[c]}$                 | 32.64 (0.07)              |

$^{[a]}$ Distance was measured between two adjacent diazaphenalenyl-subunits. $^{[b]}$ Torsion angle was measured between both diazaphenalenyl-subunits of one molecule. $^{[c]}$ 5c co-crystallized with chloroform, but displaying close packing between pairs of molecules.
This reaction sequence corresponds to the mechanism, Würthner et al. have proposed for the corresponding PDI-systems[54]. Notably, the isomerization barrier of the W/C252rthner et al. have proposed for the corresponding PDI-systems is very similar to that reported for the PDI-Cl4, which suggests that indeed the PDI-core possesses similar rigidity/flexibility as the polycyclic aromatic core of the TAPP molecules.

UV/Vis absorption and emission spectra

The UV/Vis absorption and emission spectra of the TAPP derivatives 5a–d recorded in THF are displayed in Figure 4. Similar to the non-twisted ortho-substituted TAPP derivatives, the absorption and emission maxima remain unchanged upon variation of the alkyl-substituents in the 2- and 9-positions.[42]

All derivatives were found to exhibit absorption maxima in the range of 468 to 474 nm with vibrational progressions and emission maxima in the range of 496 to 505 nm. As TAPPs are known to aggregate in solution, measurements were repeated in different solvents (DCM and CHCl3) and in different concentrations. However, identical absorption and emission data were observed, leading to the conclusion, that these twisted TAPPs do not tend aggregate in common organic solvents. An overview of the optical properties is given in Table 3.

Complementing the measurement of the absorption and emission spectra in solution, Table 3 contains vertical transition energies computed at time-dependent density functional theory (TDDFT) level of theory. While the absolute values of the vertical excitation (VE) and the vertical de-excitation (VD) energies deviate from the measured absorption and emission bands by 0.05 and 0.15 eV, respectively, the table confirms that the photophysical data remain unaffected by the variation of substituents in the 2- and 9-positions.

Since computed vertical electronic transition energies cannot be directly related to the experimental results, we also simulated vibrationally resolved adiabatic transitions.[48] Simulated absorption and emission spectra of 5d are displayed in Figure 5. At zero temperature, the simulated spectra show distinct transitions for individual vibronic transitions.

The spectra do not seem to be dominated by the 0–0 transition and they thus display a Stokes shift of 0.02 eV (140 cm–1) at zero temperature, however, the incorporation of temperature effects leads to a Stokes shift of about 0.07 eV (about 586 cm–1) at 300 K. The finite-temperature spectrum furthermore reproduces the general shape of the experimental spectra as shown in Figure 4, which is characterized by a pronounced vibrational progression at lower wavelength for the absorption but only a broadened band for emission. We note that the experimentally observed Stokes shifts are larger compared to the simulated values, which might be due to solvation effects which are not included in the simulations in vacuum.

Redox properties

To assess the redox chemical properties of the bay-chlorinated TAPP derivatives cyclic voltammograms (CVs) of all compounds were recorded. They were found to exhibit two individual and fully reversible one-electron reduction steps to the mono-anionic radical species and the subsequent di-anionic compound. In Figure 6, the CV is shown for compound 5b.

The energies of the lowest unoccupied molecular orbital (LUMO) were estimated by subtraction of the reversible first reduction potentials from the cyclic voltammograms of

Table 2. Computed relative energies including the zero-point vibrational energy (ZPVE) and angles of intermediates and the transition state (TS) structure.

| Structure | $E_{ZPVE}$ [kcal mol$^{-1}$] | Torsion angle [°][a] | Imaginary frequency [cm$^{-1}$] |
|-----------|-----------------------------|---------------------|------------------------------|
| trans-oriented enantiomer | 0 | 32 | |
| TS | 24 | 10/31 | 74.96 |
| syn-oriented intermediate | 9 | 23 | |

[a] Torsion angle was measured using the four C-atoms in the bay-area.

Table 3. Photophysical properties of 5a–d measured in THF and computed vertical electronic excitation (VE) and de-excitation (VD) energies.

| R  | $\lambda_{abs}$ [nm] (log $\varepsilon$)[a] | $\lambda_{em}$ [nm] (g$^{0.03}$)[b] | 0–0 Transition [nm][c] | Stokes shift [cm$^{-1}$] | $\lambda_{VE}$ [nm] (DFT)[d] | $\lambda_{VD}$ [nm] (DFT)[d] |
|----|---------------------------------|-------------------------------|-------------------|-------------------|-----------------|-----------------|
| 5a | CF1 | 471 (4.57) | 496 (0.12) | 482 | 1070 | 481 | 534 |
| 5b | CF1 | 472 (4.64) | 505 (0.09) | 485 | 1364 | 482 | 535 |
| 5c | C6F5 | 474 (4.59) | 496 (0.10) | 484 | 936 | 482 | 536 |
| 5d | H | 468 (3.98) | 501 (0.05) | 480 | 1407 | 478 | 532 |

[a] Absorption and emission spectra were recorded in THF. (b) 0–0-Transition was obtained of the intersection of absorption and emission spectra. [c] Vertical electronic excitation (VE) and de-excitation (VD) energies were calculated using B3LYP as functional and TZVPP as the basis set.
the redox potential of ferrocene (4.8 eV for Fc/FC$^+$). As expected, the substituents in the 2- and 9-position have only limited influence on the frontier orbitals, similar to the UV/Vis absorption and emission spectra discussed above. This was backed up by the computational determination of the Kohn–Sham frontier orbital energies determined by DFT.

Whereas the energies of the LUMO and the highest occupied molecular orbital (HOMO) of derivatives 5a–c are almost identical at around −4.15 eV, the “removal” of the perfluorinated alkyl group leads to an increase of both the HOMO and LUMO energies by about 0.5 eV, resulting in a virtual identical HOMO–LUMO gap of all derivatives. Visualization of the frontier orbitals (Figure 7), reveals the nodal planes of the frontier orbitals along the principal molecular axis in which the substituents in the 2- and 9-positions are located. This also explains the nearly identical absorption and emission spectra of 5a–d which are dominated by the HOMO–LUMO transition.

For the perfluorinated alkyl groups electron affinities between 3.21 and 3.31 eV were found for 5a–c, whereas the hydrogen-substituted compound 5d was found to possess a significantly reduced electron affinity of about 2.73 eV (Table 4). These adiabatic EA values do not differ significantly from vertical EA values obtained from GW methods (The GW method is a way to correct artefacts in Kohn–Sham (KS) methods which employ exchange-correlation (XC) functionals), see Table 2, which indicates that the one-electron reduction does not induce a significant change in the molecular geometry. This corresponds to a small reorganization energy which is desira-
ble for electron transporting compounds with large \( \lambda_r \) (reorganization energy for hole transport) and small \( \lambda_v \) (reorganization energy for electron transport). The two individual one-electron reduction steps occurring consecutively were monitored for 5a by UV/Vis spectroscopy in a spectroelectrochemical cell (Figure 8). By applying a potential of \(-0.5\) V the absorption band at 474 nm of the neutral compound completely disappeared, while the formation of a compound completely disappeared, while the formation of a species with a long-wavelength absorption maximum at 663 nm was detected. This can be attributed to the monoa-
genic radical TAPP.

For electron transporting compounds with large \( \lambda_r \) (reorganization energy for hole transport) and small \( \lambda_v \) (reorganization energy for electron transport), the absorption band to 663 nm. The spectra exhibit relatively significant further conversions.

The two reduced TAPP species, TAPP\(^{2-}\) and TAPP\(^{3-}\), of 5a–c could also be isolated quantitatively by addition of one or two equivalents of KC\(_8\) respectively (Scheme 5). The radical monoanionic radical TAPP\(^{2-}\). The further lowering of the reduction potential to \(-1.0\) V led to the second reduction step, observable by a change of color to purple and the hypsochromic shift of the absorption band to 663 nm. The spectra exhibit relatively well defined isosbestic points at 400 nm and 495 nm, indicating that both reduction steps proceed cleanly and without significant further conversions.

The two reduced TAPP species, TAPP\(^{2-}\) and TAPP\(^{3-}\), of 5a–c could also be isolated quantitatively by addition of one or two equivalents of KC\(_8\) respectively (Scheme 5). The radical monoanionic radical TAPP\(^{2-}\) compounds were characterized by EPR (Figure 9), which for all derivatives possess a \( g \)-factor of 2.004, which is to be expected for radical organic compounds. Unfortunately, hyperfine couplings were only partially resolved precluding a complete simulation of the spectra.

None of the radical monoanions showed any signs of degradation under inert atmosphere, and even under ambient conditions the radicals only degraded very slowly, over a period of weeks, in the solid state. The insertion of the second electron led to a diamagnetic species, which allowed the compounds to be characterized by standard NMR methods, performed exemplarily for compound 5a. Both \(^1\)H NMR spectra and \(^19\)F NMR spectra display a shift of their signals to a higher field probably due to the enhanced electronic shielding by the additional electrons (Supporting Information). Also, the UV/Vis absorption spectra were recorded for each species, which reproduced the results of the spectroelectrochemical investigation depicted in Figure 8 (Supporting Information).

**Bay-chlorinated TAPPs as n-channel semiconductors**

Ortho-substituted TAPP derivatives have been successfully employed as semiconductors in n-channel organic TFTs, exhibiting electron mobilities of up to 0.17 cm\(^2\) V\(^{-1}\) s\(^{-1}\). In analogy, the bay-substituted TAPPs 5a–c were evaluated in bottom-gate, top-contact TFTs with a vacuum-deposited semiconductor layer (Table 5). The TFTs consisted of a doped silicon substrate that also served as a common gate electrode, a stack of thermally grown SiO\(_2\), atomic-layer-deposited Al\(_2\)O\(_3\) and a self-assembled monolayer (SAM) of \( n \)-tetradecylphosphonic acid as the gate dielectric, and shadow-mask-patterned Au top contacts (a detailed description of the fabrication process can be

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**Table 4.** Adiabatic electron affinities (aEA) obtained from the \( \Delta^3\)SCF approach, vertical electron affinities (vEA) from the GW method, and frontier orbital energies of compounds 5a–d.

| R   | aEA (LUMO) [eV] | vEA (GW) [eV] | \( E_\text{HOMO} \) (DFT) [eV] | \( E_\text{LUMO} \) (DFT) [eV] | \( E_\text{HOMO} \) (GW) [eV] | \( E_\text{LUMO} \) (GW) [eV] |
|-----|----------------|---------------|------------------|------------------|------------------|------------------|
| 5a  | CF\(_3\) | 3.23 | 3.21 | -6.84 | 2.71 | -4.12 | 2.72 |
| 5b  | CF\(_3\) | 3.22 | 3.25 | -6.86 | 2.71 | -4.15 | 2.72 |
| 5c  | CF\(_3\) | 3.31 | 3.27 | -6.91 | 2.71 | -4.20 | 2.72 |
| 5d  | H   | 2.73 | 2.75 | -6.43 | 2.72 | -3.71 | 2.93 |

[a] Properties were calculated using B3LYP as the functional and a def2-QZVPP as basis set. [b] LUMO energy was estimated from the reversible first reduction potentials obtained from the cyclic voltammograms using the redox potential of ferrocene as reference (4.8 eV for Fc/Fc\(^+\)).

![Figure 8. Absorption spectra of the two individual reduction steps of 5a in THF; voltage steps from 0 V (black) via \(-0.5\) V (red) to \(-1.0\) V (orange).](image1)

![Figure 9. EPR-spectrum (THF, r.t.) of 5b.](image2)

![Scheme 5. Reduction of 5a–c to the radical monoanionic (5a–c\(^{2-}\)) or diamagnetic dianionic TAPP (5a–c\(^{3-}\)) using KC\(_8\).](image3)
To further understand the different influence of ortho- and bay-substitution in TAPP derivatives, the two core-chlorinated TAPP isomers $5\text{c}$ and II shall be compared. The absorption maxima at 474 nm ($5\text{c}$) and 469 nm (II) of both isomers indicate that the bathochromic shift, induced by the chlorine substitution, is almost equally pronounced (Figure 11). However, the emission maximum of the $5\text{c}$-substituted derivative is red-shifted by 15 nm compared to the ortho-substituted TAPP, resulting in a Stokes shift for $5\text{c}$ of 936 cm$^{-1}$ which is almost twice as large as observed for II (445 cm$^{-1}$). Additionally, the high fluorescence quantum yield of the ortho-chlorinated II (0.78) is reduced to 0.10 for the twisted bay-chlorinated TAPP $5\text{c}$ which appears to be characterized by more accessible internal degrees of freedom and thus enhanced non-radiative relaxation processes.

The comparison of the electrochemical properties also reveals some significant differences between $5\text{c}$ and II (Figure 12). The LUMO-level of both chlorinated isomers at $-4.20$ eV ($5\text{c}$) and $-4.03$ eV (II) is significantly stabilized compared to the unsubstituted compound I (−3.66 eV), however, this effect is even more pronounced for the bay-substituted TAPP $5\text{c}$. In contrast to the ortho-chlorinated derivative II, the bay-substitution additionally leads to a stabilization of the HOMO level, leading again to similar HOMO–LUMO gaps of $2.70$ eV ($5\text{c}$) and $2.63$ eV (II). The electron affinity, which is also a key parameter in the evaluation of potential n-channel semiconductors, is higher for the bay substitution (3.31 eV) compared to the ortho substitution (3.09 eV). Overall, bay-chlorination leads to a greater stability of the anionic (radical) species compared to the ortho-substituted constitutional isomers.

Whereas both, the photophysical and the electronic properties are similar for both TAPP-Cl isomers, the change of molecular geometry resulting from the different substitution patterns, is significant. Whereas the planar peropyrene core is barely affected by the ortho-substitution, the steric repulsion of the bay substituents leads to a large twist of approximately 30 degrees between the two subunits of the TAPP. This difference in molecular structure gives rise to an organized and dense packing pattern in case of the ortho-substituted derivative II in its solid-state structure (with intermolecular distances

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**Table 5.** Summary of the transistor parameters electron field-effect mobility ($\mu_{\text{on}}$), on/off current ratio ($I_{\text{on}}/I_{\text{off}}$), threshold voltage ($V_{\text{th}}$), subthreshold swing ($SS$) and temperature ($T$) measured under ambient conditions.

| $5\alpha$ | $I_{\text{on}}/I_{\text{off}}$ | $V_{\text{th}}$ [V] | $SS$ [V dec$^{-1}$] | $T$ [°C] | $\mu_{\text{on}}$ [cm$^2$ V$^{-1}$ s$^{-1}$] |
|----------|-------------------------------|---------------------|----------------------|---------|----------------------------------|
| $5\beta$ | 10$^6$                         | 6                   | 1.9                  | 70      | 0.002                            |
| $5\gamma$| 10$^6$                        | 19                  | 2.8                  | 40      | 0.003                            |
| $5\delta$| 10$^6$                        | 13                  | 4.4                  | 90      | 0.001                            |

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![Figure 10. Atomic force microscopy (AFM) images of vacuum-deposited films of $5\alpha$ (left), $5\beta$ (middle) and $5\gamma$ (right).](image)

![Figure 11. Absorption spectra of unsubstituted TAPP I (red), ortho-chlorinated TAPP II (blue) and bay-chlorinated TAPP $5\gamma$ (black) in THF.](image)

![Figure 12. Calculated HOMO- and LUMO-levels (left) and HOMO–LUMO-gaps and EA (right) of I, II and $5\gamma$.](image)
of 3.38 Å, whereas this type of packing is disrupted for the bay-substituted derivative 5c leading to reduced electron mobilities while the molecular redox properties are virtually unchanged. Conversely, the reduced long-range order, leads to a significantly increased solubility and potential processability of the bay-substituted molecules.

Conclusions

In this study we have expanded the chemistry of tetraazapero-
pyrenes (TAPPs) to include non-planar bay-chlorinated derivatives. This required a new synthetic strategy which was based on previous work in perylene chemistry and required the introduction of the condensed pyrimidine units to the central perylene core in the final reaction steps. As expected from previous studies of perylene bisimides, the bay-chlorinated TAPPs possess a twisted aromatic core due the steric pressure of the bay-substituents. In contrast to the previously studies of perylene bisimides, the bay-chlorinated TAPPs allowed facile reduction of ortho-substituents. In contrast to the previously studies of perylene bisimides, the bay-chlorinated TAPPs allowed facile reduction of ortho-substituents. Further reduction gave thermally stable dianionic species which were characterized in solution. Both anionic species were characterized by UV/Vis, EPR and NMR spectroscopy, and theoretical modelling. The present work allows for the first time not only to fine-tune the electronic properties of TAPPs, but simultaneously adjust the geometric properties in a complementary fashion.

Experimental Section

The syntheses were performed under dried argon in standard Schlenk glassware, which was flame-dried prior to use. Solvents were dried according to standard procedures. The 1H-, 13C- and 19F-NMR spectra were recorded with Bruker AVANCE 400 and 600II+ spectrometers equipped with variable-temperature units. 1H signals (CDCl3: 7.26 ppm, [D6]THF: 1.72 ppm/3.58 ppm, [D6]DMSO: 2.50 ppm) and 13C-signals (CDCl3: 77.16 ppm, [D6]THF: 67.21 ppm/25.31 ppm, [D6]DMSO: 39.52 ppm) were referenced according to standard literature values. The MALDI mass spectra were obtained from a Bruker apex-Qe FT-ICR spectrometer and a Bruker Autoflex Speed MALDI-TOF spectrometer. The absorption spectra were recorded on a Cary 500 UV/Vis/NIR spectrophotometer and were baseline and solvent corrected. Emission spectra were measured on a Varian Cary Eclipse Spectrophotometer. Description how Fluorescence quantum yields were obtained is explained in detail in the Supporting Information. Cyclic voltammetry was conducted using a standard commercial electrochemical analyser in a three-electrode single-component cell under inert atmosphere. The reaction mixture was filtered over Celite and the solvent was removed in vacuo to give the product 3 as a green solid (0.72 mg, 1.67 mmol, 97 %). 1H NMR (600.13 MHz, [D6]THF, 295 K): δ [ppm] = 7.30 (s, 4H), 9.19 (bs, 4H), 10.48 (bs, 2H). 13C NMR (150.90 MHz, [D6]DMSO 295 K): δ [ppm] = 113.4, 123.5, 125.8, 130.7, 136.6, 136.7.

Preparation of compound 2

3,4,9,10-Tetrabromo-1,6,7,12-tetrachloroperylene (200 g, 2.83 mmol, 1 equiv.) was suspended in THF (200 mL) and n-butyl-lithium (7.94 mL, 2.5 M in hexane, 19.8 mmol, 7 equiv.) were added dropwise at −78 °C. After stirring at this temperature for one hour a solution of Tosyl azide (5.59 g, 28.4 mmol, 10 equiv) in THF (5 mL) was added dropwise and the reaction mixture was allowed to warm up to r.t. overnight. After the addition of H2O (30 mL), the phases were separated and the aqueous phase was extracted with DCM (3 × 100 mL). The united organic phases were dried over Na2SO4 and evaporation of the solvent gave the crude product, which was further washed with MeOH, acetonitrile and pentane to yield 2 as a red solid (0.75 g, 1.53 mmol, 66 %). 1H NMR (600.13 MHz, CDCl3, 295 K): δ [ppm] = 7.35 (s, 4H). 13C NMR (150.90 MHz, CDCl3, 295 K): δ [ppm] = 114.6, 119.4, 122.1, 133.6, 136.6, 136.7.

Preparation of compound 3

Sodium borohydride (0.221 g, 5.85 mmol, 2.7 equiv) was added to a solution of 2 (1.20 g, 2.17 mmol, 1 equiv) in THF (72 mL) and MeOH (6 mL). The reaction mixture was stirred at r.t. for two hours. The reaction was quenched by the addition of 2m HCl (1.20 mL), stirred for 30 minutes and subsequently aqueous 2M NaOH (1.20 mL) was added. The solvent was removed in vacuo and the remaining solid was washed with water, MeOH, acetonitrile and pentane and dried in vacuo to give 3 as a red solid (0.75 g, 1.67 mmol, 77 %). 1H NMR (600.13 MHz, [D6]THF, 295 K): δ [ppm] = 5.43 (s, 8H), 6.65 (s, 4H). 13C NMR (150.90 MHz, [D6]DMSO 295 K): δ [ppm] = 113.4, 123.5, 125.8, 136.4, 146.5, 159.5. HRMS (MALDI-MSI): calcd for C24H4O3Cl3F6N4 [M]+: 603.9787, found: 603.9781.

Preparation of compound 4

MnO2 (3.00 g, 34.5 mmol, 20.7 equiv) was added to a solution of 3 (0.75 g, 1.67 mmol, 1 equiv) in THF (250 mL). After stirring for one hour at r.t., the reaction mixture was filtered over Celite and the solvent was removed in vacuo to give the product 3 as a green solid (0.72 mg, 1.67 mmol, 96 %). 1H NMR (600.13 MHz, [D6]DMSO, 295 K): δ [ppm] = 7.30 (s, 4H), 9.19 (bs, 4H), 10.48 (bs, 2H). 13C NMR (150.90 MHz, [D6]DMSO 295 K): δ [ppm] = 101.2, 122.8, 125.0, 134.6, 158.2. HRMS (MALDI-MSI): calcd for C20H10Br3Cl3F6N4 [M]+: 449.9787, found: 449.9781.

Preparation of compound 5a

Triethylamine (435 μL, 3.12 mmol, 2.8 equiv) and trifluoroacetic anhydride (374 μL, 2.79 mmol, 2.5 equiv) were added to a solution of DPDi-Cl (4) (500 mg, 1.12 mmol, 1 equiv) in THF (10 mL) and the reaction mixture was refluxed for 72 h. After cooling to r.t., the volatiles were removed in vacuo and the crude mixture was separated by column chromatography (petroleum ether/ethyl acetate 10:1) to give the product 5a as a yellow solid (75 mg, 124 μmol, 11 %). 1H NMR (600.13 MHz, CDCl3, 295 K): δ [ppm] = 8.74 (s, 4H). 13C NMR (150.90 MHz, CDCl3, 295 K): δ [ppm] = 110.2, 122.8, 125.0, 134.6, 158.2. HRMS (MALDI-MSI): calcd for C8H6F2Cl3I3 [M]+: 603.9065; found: 603.9059.

Redox potentials measured against SCE in THF: Ered1 = −0.18 V; Ered2 = −0.49 V.

Chem. Eur. J. 2019, 25, 14669 – 14678 www.chemeurj.org 14676 © 2019 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim
Preparation of compound 5b:
Triethylamine (217 µmol, 1.56 mmol, 2.8 equiv) and perfluorobutyryl chloride (207 µl, 1.39 mmol, 2.5 equiv) were added to a solution of DPDI-Cl (4) (250 mg, 0.56 mmol, 1 equiv) in THF (10 mL) and the solution was refluxed for 72 h. After cooling to r.t., the volatiles were removed in vacuo and the residue was washed thoroughly with water (200 mL). The crude compound was recrystallized in hot ethanol to afford 5b as a yellow solid (170 mg, 76%). UV/Vis spectroscopy (petroleum ether/ethyl acetate 10:1) was detected due to coupling to fluorine groups. 19F NMR (376.27 MHz, CDCl 3 295 K): δ (ppm) = −80.1 (t, JF,F = 9.03 Hz, 6 F), −114.0–114.1 (m, 4 F), −125.4 (bs, 4 F). HRMS (MALDI−): calcd for C28H40F10Cl2N4·: 803.8937; found: 803.8932. Redox potentials measured against SCE in THF: E:red1 = −0.19 V; E:pol2 = −0.49 V.

Preparation of compound 5c:
Triethylamine (414 µL, 2.97 mmol, 2.8 equiv) and pentfluoroproionic anhydride (526 µL, 2.66 mmol, 2.5 equiv) were added to a solution of DPDI-Cl (4) (476 mg, 1.06 mmol, 1 equiv) in dioxane (10 mL) and the solution was refluxed for 72 h. After cooling to r.t., the solvent was removed in vacuo and the residue was washed thoroughly with water (200 mL). The crude compound was recrystallized in hot ethanol to afford 5c as a yellow solid (25 mg, 0.053 mmol, 24%). 1H NMR (600.13 MHz, CDCl 3 295 K): δ (ppm) = 8.76 (s, 4 H). 13C NMR (150.90 MHz, CDCl 3 295 K): δ (ppm) = 112.6, 125.3, 126.1, 130.8, 141.3, 153.8, 156.1. Residual 13C-signals of the N-C-N- and perfluorinated propyl-groups could not be detected due to coupling to fluorine groups. 19F NMR (376.27 MHz, CDCl 3 295 K): δ (ppm) = −81.4 (t, JF,F = 1.75 Hz, 6 F), −116.0 (bs, 4 F). HRMS (MALDI−): calcd for C46H45F33Cl3N4·: 865.8883; found: 865.8879. Redox potentials measured against SCE in THF: E:red1 = −0.681 V; E:pol2 = −0.383 V.

Preparation of compound 5d:
DPDI-Cl (4) (100 mg, 0.223 mmol, 1 equiv) was dissolved in 5 mL triethylthiophosphate and 1 mL of formic acid was added. The solution was stirred for 3 d at 110 °C. After cooling to r.t., the volatiles were removed in vacuo and the residue was washed with water, MeOH and pentane. The pure compound 5d was isolated as a yellow powder (25 mg, 0.053 mmol, 24%). 1H NMR (600.13 MHz, CDCl 3 295 K): δ (ppm) = 10.01 (s, 2 H), 8.59 (s, 4 H). 13C NMR could not be measured due to low solubility. HRMS (MALDI−): calcd for C28H40F10Cl2N4·: 847.9323; found: 847.9315. Redox potentials measured against SCE in THF: E:red1 = −0.681 V; E:pol2 = −0.383 V.

Theoretical methods
Frontier orbitals and electron affinities: The DFT calculations to obtain orbital energies and electron affinities were carried out using ORCA 4.0.1 program package.[65] B3LYP was employed as functional.[66,67] a def2-SVP basis set was used for all atoms during geometry optimizations.[68,69] Every optimization was verified by frequency calculations. All other properties were calculated using a def2-QZVP basis set.[70]
Vertical transitions: Calculations of the vertical excitation energies (VEE) and vertical de-excitation energies (VDE), employing B3LYP together with the def2-TZVP basis, have been carried out using the Turbomole program package V7.2[71,72] using default convergence criteria for both the response equations and the geometry convergence. Accurate geometries for the Franck-Condon simulations were obtained with tightened thresholds of 10−9 and employing Dz symmetry.[65] The calculations of the vibronic (Franck-Condon) spectra were conducted using the HOTFCHT program.[73–75]

Interconversion energies: The geometries and their relative energies have been computed using the Turbomole program V7.2. PBE0 was employed as functional together with def2-TZVP basis and the RI approximation (RI-J). The stationary points were verified with analytical second derivatives.

Acknowledgements
This work has been supported by the Deutsche Forschungsgemeinschaft (DFG) within the collaborative research centre SFB1249 “N-Heteropolycycles as Functional Materials” (Projects A02, B07, and C01). Open access funding enabled and organized by Projekt DEAL.

Conflict of interest
The authors declare no conflict of interest.

Keywords: halogenos · perylenes · radicals · synthetic methods · UV/Vis spectroscopy

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