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Core-Extended Terrylene Tetracarboxdiimide: Synthesis and Chiroptical Characterization

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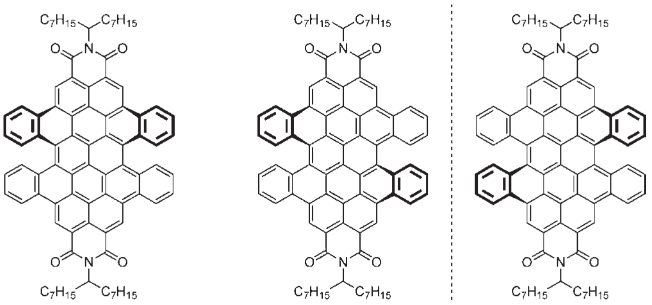
ABSTRACT



The novel 1,16:6,7:8,9:14,15-tetranaphthoterrylene tetracarboxdiimide was synthesized via a straightforward route, yielding optically active atropisomers with a high racemization barrier. Absorption, fluorescence, and circular dichroism measurements revealed high absorption coefficients and fluorescence quantum yields and enabled the stereochemical assignment in combination with quantum mechanical calculations.

Among various classes of chiral substances atropisomeric chromophores represent an intensively studied field in organic chemistry as those compounds can be used in various pharmaceutical,[1] catalytic,[2] or organic electronic applications.[3] However, their conformational stability remains a challenge and most examples are limited to biphenyl or binaphthyl derivatives.[4] Some perylene tetracarboxdiimides for instance are reported to form stereoisomers, but in most cases the racemization energy barrier is too low to obtain enantiomerically pure compounds.[5] In order to inhibit interconversion of these isomers, bulky or rigid substituents have to be attached to the *bay*-positions of the perylene core.[6] Nevertheless such compounds are promising candidates for organic electronics[7] and chiral self-recognition[8] due to their preference to undergo

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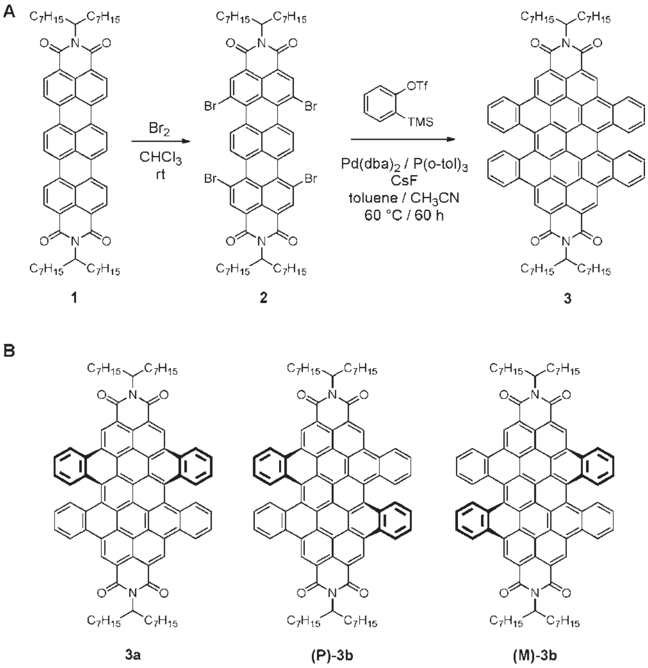
homochiral π–π-stacking.[9] Analogous research involving higher homologues of PDI such as terrylene diimide (TDI) has not been reported up to now, although remarkable optical and electronic[10] behavior can be observed for the latter and an implementation of axial chirality should be easily possible via *bay*-functionalization as well. Herein we present the synthesis and characterization of 1,16:6,7:-8,9:14,15-tetranaphthoterrylene tetracarboxdiimide **3**, which combines the advantages of an atropisomeric chromophore and a core enlarged TDI. In contrast to known PDI derivatives, even the unsubstituted isomers show a high conformational stability enabling complete enantiomeric separation.

Scheme 1. (A) Synthesis of Tetranaphtho-TDI **3** via Annulation of Tetrabromo-TDI **2**; (B) Possible Conformers of **3**



The synthesis of the tetranaphtho-TDI **3** starts from the established terrylene diimide **1**,[11] which is at first subjected to bromination with bromine in chloroform to yield **2**. The key reaction step consists of a 4-fold palladium catalyzed benzannulation of the tetrabromo-TDI **2** with *o*-trimethylsilyl-phenyltriflate in toluene and acetonitrile at 60 °C (Scheme 1A). Similar conditions are already known from the *bay*-extension of PDI and QDI derivatives.[12] According to theoretical calculations (GAUSSIAN 03W, DFT), the sterical hindrance of the neighboring benzene rings induces a twist within the molecules with torsion angles of about 45° (**3a**) and 50° (**3b**) respectively (Figure 1).

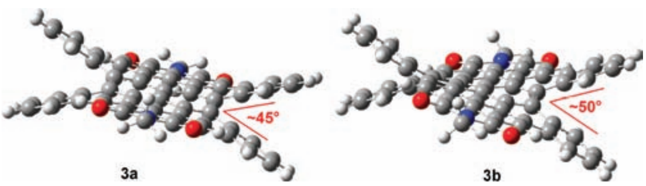


Figure 1. Illustration of the conformational difference of **3a** and **3b** (GAUSSIAN 03W, DFT).

For this reason, three possible isomers can be expected. The two diastereomers **3a** and **3b** can be separated via standard silica chromatography, **3b** consisting of the two atropo-enantiomers **(P)-3b** and **(M)-3b** as shown in Scheme 1B.[13] The assignment of the diastereomers was done by means of chiral HPLC. Herein isomer **3b** produces two signals in the chromatogram originating from the atropisomers (P and M), which can be isolated accordingly (Figure 2).

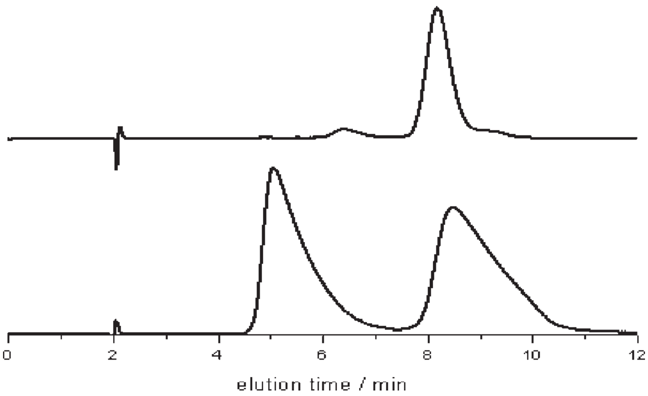


Figure 2. HPLC chromatograms of **3a** (top) and **3b** (bottom) on a Kromasil Chiral DMB column using THF/*n*-hexane (5:95) as eluent.

The UV/vis absorption measurements of both diastereomers **3a** and **3b** reveal a hypsochromic shift of about 90 nm relative to the parent terrylene tetracarboxdiimide,[14] resulting in absorption maxima at 566 nm (**3a**) and 557 nm (**3b**) with absorption coefficients of about 70 000 M^{-1} cm^{-1} (Figure 3A and 3B). At the same time the typical vibronic fine structure of the TDI is maintained in the long wavelength area. An analogous behavior was already reported for bay extended perylene and quaterrylene tetracarboxdiimides.[9] Comparing the absorption spectra of **3a** and **3b**, a difference in the λ_{max} of 9 nm is observed, owing to the contrast of the s-shaped bending of **3a** and the

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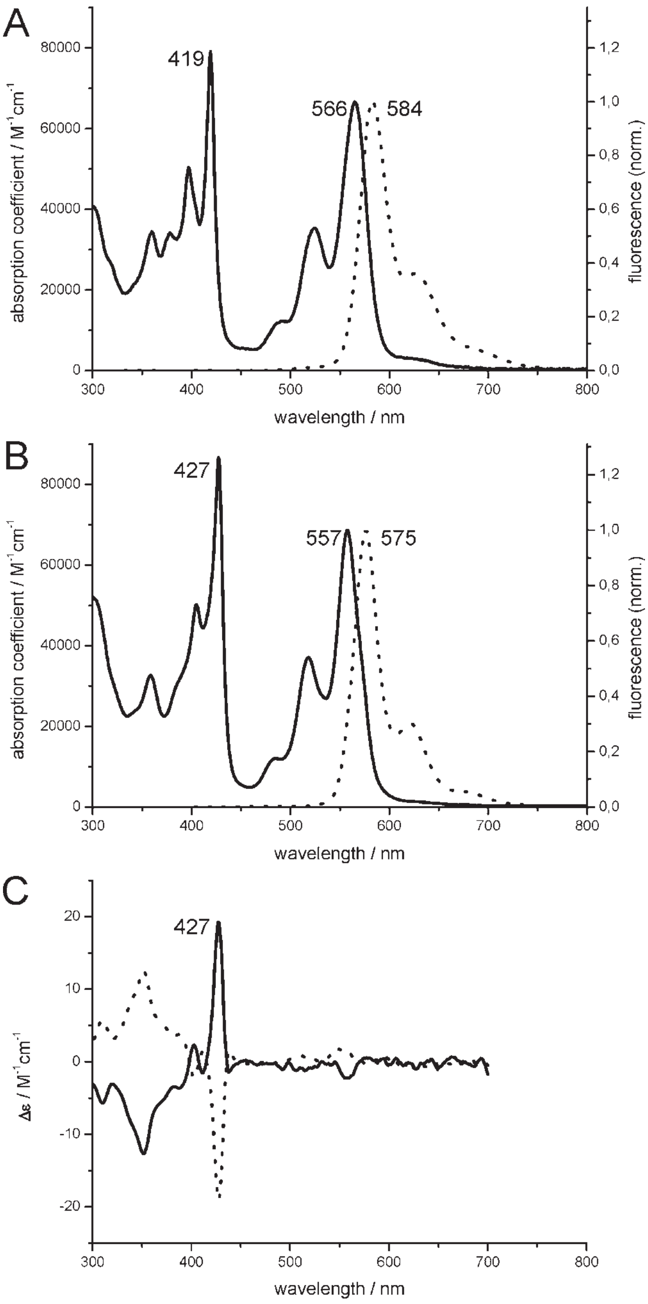

Figure 3. (A) Absorption (solid) and emission spectrum (dotted) of **3a**. (B) Absorption (solid) and emission spectrum (dotted) of **3b**. (C) CD spectra of **(P)-3b** and **(M)-3b**. Solid line: First eluted enantiomer. Dotted line: Second eluted enantiomer (toluene, 20 °C, fluorescence excitation $\lambda_{ex} = 550$ nm).

screw-shaped twist of **3b** (Figure 1). As a result the fluorescence spectroscopy shows emission at 584 and 575 nm respectively with a fluorescence quantum yield of 48% (Figure 3A and 3B).

Furthermore circular dichroism spectroscopy was applied to evaluate the chiroptical properties of the enantiomers **(P)-3b** and **(M)-3b**. Figure 3C demonstrates the expected mirror symmetry of the respective spectra. In the visible region of the CD spectra, a sharp peak at 427 nm and a maximum at 352 nm are observed showing opposite Cotton effects. These bands can be partially assigned to transitions from the HOMO to the third LUMO (LUMO+2) and to the fifth LUMO (LUMO+4) respectively (Figure 4). DFT calculations (GAUSSIAN 03W)[15] reveal the location of these orbitals along the short molecular axis. As the tilting of the naphtho-groups in this direction represents the origin of the atropisomerism, optical activity is observed consequentially for the corresponding wavelength range. In contrast to that the HOMO and LUMO orbitals show a predominant presence at the long molecular axis. The weakness of the CD signals in the region of the HOMO−LUMO transition (500−600 nm) therefore reflects the achirality of the TDI core. Upon stepwise heating up to 80 °C the measurements did not show any mentionable temperature dependence of the CD spectrum. Only a slight decrease of about 8% of the $\Delta\varepsilon$ values was observed after 6 h at 80 °C in toluene, resulting in a half-lifetime of approximately 49 h and a free activation enthalpy of $\Delta G^{\#} = 121.4 \pm 0.3$ kJ/mol for this condition. These results are comparable to those of strongly

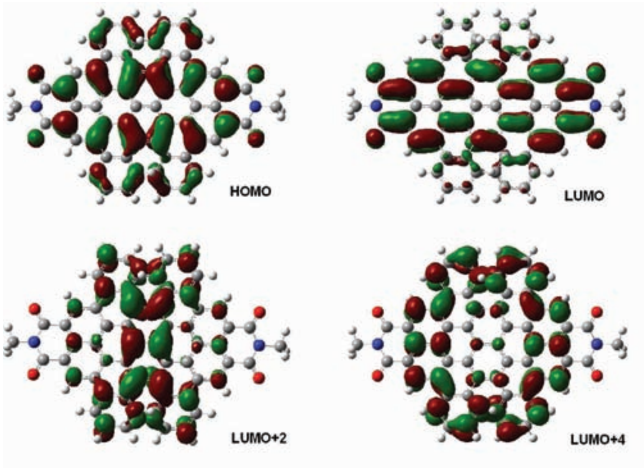

Figure 4. Molecular orbitals of tetranaphtho-TDI **3** according DFT calculations (GAUSSIAN 03W). Abbreviations: HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

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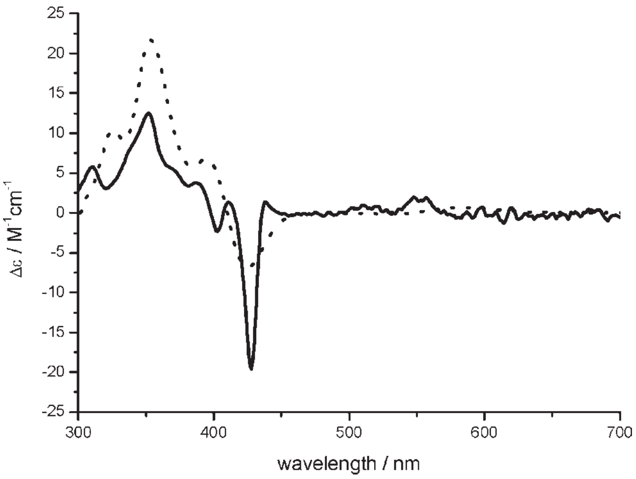

Figure 5. Comparison of the CD spectrum of the second eluted enantiomer in toluene (solid line) and the calculated spectrum of **(P)-3b** (dotted line, GAUSSIAN 03W, TD-SCF/DFT).

sterically hindered 1,8-biarylnaphthalenes[16] and even higher than the respective results of the related 1,6,7,12-tetrasubstituted perylene tetracarboxdiimides.[6a]

In order to determine the absolute configuration of both stereoisomers obtained from the chiral HPLC, the recorded CD spectra were compared to quantum chemical calculations. For this purpose the respective geometries were determined using a DFT optimization. Subsequently the corresponding CD spectra were received by means of a TD-SCF/DFT calculation (GAUSSIAN 03W)[15] followed by processing with GaussSum (Version 2.2).[17] The results are presented in Figure 5. Apparently the simulated spectrum of **(P)-3b** shows a sufficient agreement with the experimental data of the second eluted enantiomer. Both calculations show the same mirror-symmetric behavior which was already observed for the real CD spectra. The first eluted stereoisomer can therefore be assigned to the (M)-configuration.

In summary we presented the synthesis of tetranaphtho-TDI **3**, a novel bay-extended terrylene tetracarboxdiimide. Starting from known TDI the straightforward route provides the final compound in only two steps. The three observed isomers formed within the reaction could be isolated and assigned to their respective geometries. Furthermore they show a low degree of interconversion even at elevated temperatures. Optical spectroscopy including absorption, fluorescence, and circular dichroism measurements reveal defined vibronic fine structures and high absorption coefficients maintained from the TDI core in combination with an optical activity originating from the bending of the four naphtho-groups out of the molecular plane. Especially the enantiomers **(P)-3b** and **(M)-3b** are promising candidates for such demanding applications such as chiral molecular switches[7c] or single-molecule chiroptical spectroscopy[18] as they exhibit strong absorption and fluorescence of visible light together with high conformational stability, even without auxiliary substituents.

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Supporting Information Available. Full experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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