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Perylene Bisimides with Rigid 2,2′-Biphenol Bridges at Bay Area as Conjugated Chiral Platforms

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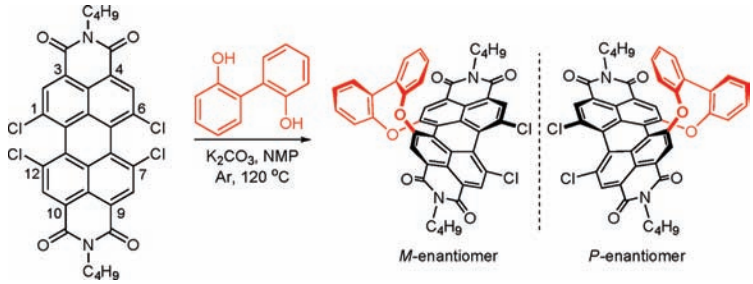
ABSTRACT



Facile nucleophilic substitution of two chlorine atoms by 2,2′-biphenol at one of the two bay areas (1,12- and 6,7-positions) of core-tetrachlorinated perylene bisimide afforded a novel, completely desymmetrized perylene bisimide building block, which could be further functionalized by substitution of the remaining two chlorine atoms. The atropisomers (*P*- and *M*-enantiomers) of the core twisted perylene bisimides were resolved by HPLC on a chiral column at room temperature, and the activation parameters for racemization were elucidated.

Natural chiral molecules such as nucleic acids, amino acids, and sugars are of vital importance for biological systems. Chiral compounds are also of great significance for chemical processes and materials science as they are widely applied in numerous fields such as chiral recognition[1] and self-assembly,[2] enantioselective catalysis,[3] nonlinear optics,[4] and as molecular switches.[5] In recent years, conjugated chiral systems have gained much attention in the field of organic materials.[6] Most prominent examples of chiral compounds with inherent chirality used in this context are biphenyl[7] and binaphthyl[8] derivatives, annelated phenylenes,[6] and helicenes and helicene-like systems.[9]

Perylene bisimides (PBIs) with functional substituents at the carbocyclic scaffold in the bay areas have attracted a great deal of attention in the past years owing to their outstanding optical, electronic, and light fastness properties and their high solubility in common organic solvents.[10] Recently, Wang et al. significantly extended the concept of bay functionalization by

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synthesizing fully conjugated triply linked di- and tri-PBIs[11] and also monobay-dichlorinated PBIs.[12]

The introduction of bay substituents endows the perylene core with a twisted π-system. It has been recognized already some years ago that such twisted PBI fluorophores might possess interesting chiroptical properties.[13] However, it is usually difficult to isolate enantiomerically pure PBIs due to the low barriers for the interconversion of the two core-twisted atropisomers in solution. The kinetic racemization process could be, in principle, prevented by increasing the size of the sterically demanding bay substituents.[14] Another strategy that was developed in our group to restrict the dynamic racemization process of tetraphenoxy-substituted perylene bismides is based on the bridging of phenoxy substituents at the bay positions with oligo(ethylene glycol) chains through macrocyclization.[15] However, this strategy suffers from the inherent difficulty of further chemical functionalization of the chiral PBI unit.

Herein we present a new approach to configurationally stable chiral PBIs, e.g., PBI **2**, bearing reactive substituents at one of the two bay areas for further functionalization. This was achieved by introduction of a rigid 2,2′-biphenol bridge at one bay area. The two adjacent phenoxyl groups are connected directly at *ortho* positions by a covalent C−C bond, which not only introduces an asymmetric structure at the bay area but also imparts rigidity to the perylene core. The rigid and twisted π-system achieved by this approach facilitates the separation of the atropo-enantiomers, and thus investigation of their chiroptical properties and elucidation of activation parameters for the racemization. The most attractive feature of this unprecedented chiral monobiphenyl-bridged PBI is the possibility for further functionalization on the other bay area, which makes it a promising conjugated chiral platform.

PBI **2** with a 2,2′-biphenoxy bridging unit at one bay area was synthesized directly from tetrachloro-substituted PBI **1** and 2,2′-biphenol (mole ratio 1:1) in 57% yield as outlined in Scheme 1. The further nucleophilic substitution of the remaining two chlorine atoms in PBI **2** with excess amount of 2,2′-biphenol afforded PBI **3** with two biphenoxy bridges. Different phenoxyl groups with functional substituents may be introduced to PBI **2** by nucleophilic substitution of the two chlorine atoms to form PBIs with unsymmetrical substitution pattern on the two bay areas. The proof-of-the-concept example of the unsymmetrical bay-substituted PBI **4** was synthesized in order to compare the optical properties of the PBIs with different rigidity.

Compared with the tetrachloro-substituted PBI **1**, its monocyclization to PBI **2** with a 2,2′-biphenoxy bridge at one bay area might introduce more rigidity, which would make the interconversion of the twisted conformers (*P* and *M*) less facile. Indeed, the enantiomers of PBI **2** are separable by HPLC on a chiral colunm (Reprosil 100 chiral-NR) at room temperature using dichloromethane as the eluent (see Figure S7 in Supporting Information). The configurations of the first and the second eluted atropisomers (retention times 4.0 and 5.3 min) are assigned as *P* and *M*, respectively, by comparing their circular dichroism (CD) spectra with those of previously reported atropisomerically pure macrocyclic PBIs (details are given in following sections).[16]

The molecular geometry of PBI **2** was optimized with HyperChem using a semiempirical method (AM1), and the results are shown in Figure 1. As can be seen in the geometry optimized structures, one phenyl ring of the biphenyl group is situated above the perylene core, while the other one extends to the side of the perylene core.[17] Accordingly, the molecular structure loses symmetry elements owing to the different substituents on two bay areas and the twisted configuration of the biphenyl unit relative to the perylene core. This structual feature is supported by ^{1}H, HH-COSY and ^{13}C NMR spectra of PBI **2** (see Supporting Information). The similar structural information was also obtained for PBI **4**. In the case of bis-biphenoxy-substituted PBI **3**, two diastereomers are expected as the two biphenyl groups may locate at the same face (denoted as *minor*-**3**) or two different faces (denoted as *major*-**3**) of the perylene core. The ^{1}H NMR spectra and semiempirical calculations indeed support the coexistence of the two diastereomers of PBI **3** (for details, see Supporting Information).

The atropo-enantiomers of PBI **2** were successfully resolved by HPLC using a semipreparative chiral column at room temperature. The CD spectra of the isolated enantiomers of PBI **2** show a clear mirror image relation as depicted in Figure 2 (bottom). In the region of 460−570 nm of the CD spectra, a broad monosignated peak with a maximum at 539 nm can be seen that nicely correlates with the absorption maximum at 545 nm (Figure 2, top). In the

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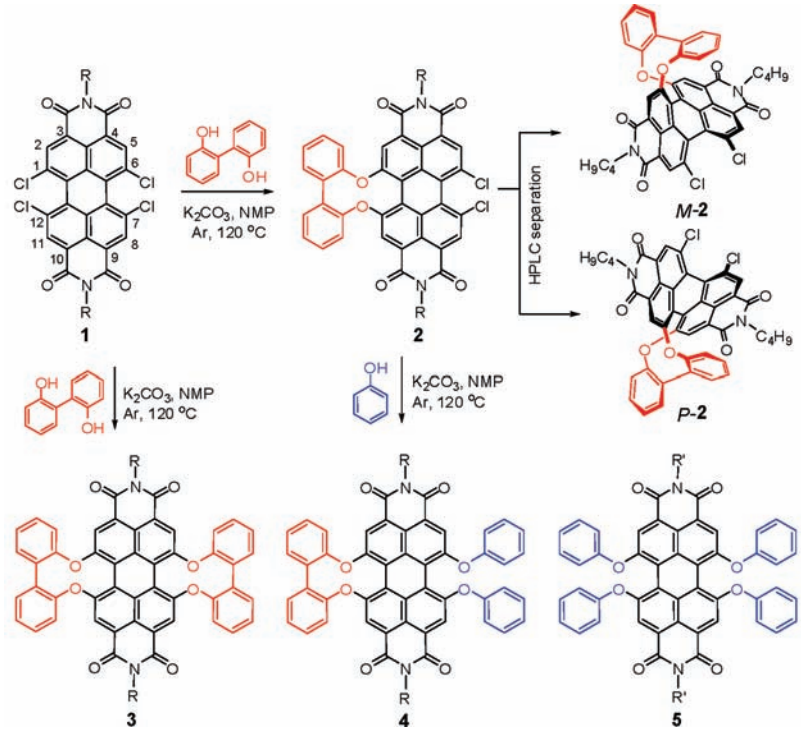
Scheme 1. Synthesis of PBIs **2**−**4**, Chiral Resolution of the Atropisomers of **2**, and Structure of Reference PBI **5**[a]



[a] R = *n*-C_4H_9; R′ = 2,6-di(*i*-Pr)Ph; NMP = 1-methyl-2-pyrrolidone.

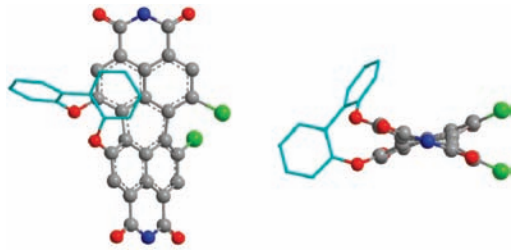


Figure 1. Geometry optimized structues of PBI **2** calculated with HyperChem using a semiempirical method (AM1). The alkyl chains and the protons are omitted for simplicity. Left: view from the top of the molecule. Right: view along the N−N direction. Only the *M*-enantiomer is shown.

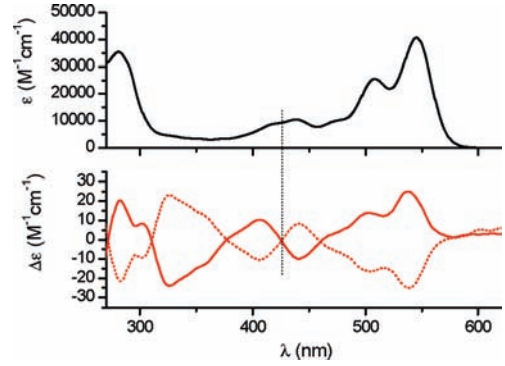


Figure 2. UV−vis absorption (top, identical for *P*-**2** and *M*-**2**) and CD spectra (bottom) of *P*-**2** (solid red line) and *M*-**2** (dotted red line) enantiomers of PBI **2** in dichloromethane at 20 °C.

CD spectral region of 460−570 nm of the enantiomers, the S_0-S_1 transition is located whose transition dipole moment is polarized along the long axis (N−N axis) of the PBI. On the basis of previously reported stereochemical assignment of atropisomerically pure macrocyclic PBI systems,[16] the positive signal for the longest wavelength transition (λ_{max} = 539 nm) in the CD spectrum of the first eluted fraction of **2** can be attributed to a right-handed helical configuration of the twisted perylene core, and thus this enantiomer can be assigned to *P*-**2**. Accordingly, the second eluted fraction with a negative Cotton effect for the longest wavelength transition can be assigned to *M*-**2**.

On the other hand, for the S_0-S_2 transition (the transition dipole is polarized along the short axis of the PBI) in the region of 375−460 nm of the CD spectra, an unsymmetric bisignated signal was observed with a negative first Cotton effect at a longer wavelength and a positive second one at a shorter wavelength for the first eluted enantiomer *P*-**2** and vice versa for the second eluted enantiomer *M*-**2**. In both cases, the peak maxima of the first Cotton effects are located at 440 nm and those of the second ones are found at about 405 nm with a crossover point at 425 nm. This zero transition corresponds well to the absorption band of the S_0-S_2 transition. Similar Cotton effects corresponding to the S_0-S_2 transition were also observed for 1,6,7,12-tetrachloro- and tetrabromo-substituted PBIs previously.[14]

The optical properties of the PBIs **3** and **4** and the reference PBI **5** were investigated by UV−vis and fluorescence spectroscopy. The UV−vis absorption spectra (Figure 3a) of PBIs

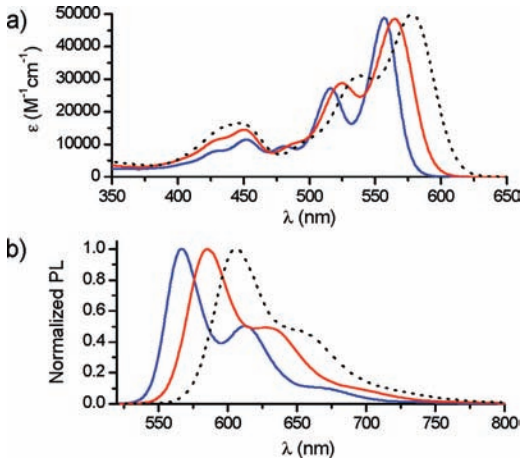


Figure 3. (a) UV−vis absorption and (b) normalized emission spectra of PBIs **3** (blue lines), **4** (red lines), and **5** (dotted lines) in dichloromethane at room temperature.

3 and **4** with mono- or dicyclization at bay area show hypsochromic shifts of the absorption maxima of the S_0-S_1 transition (~550 nm) by 20 and 12 nm, respectively, in comparison to that of PBI **5**, accompanied by pronouncedly narrowed absorption bands, indicating an increase of the rigidity of the perylene cores of PBIs **3** and **4**. Similar conclusions can be drawn from the fluorescence spectra. As shown in Figure 3b, fluorescence spectra of PBIs **3** and **4** show hypsochromic shifts with enhanced vibronic fine structure compared to that of PBI **5**. Moreover, the Stokes shifts of PBIs **3** and **4** in dichloromethane are much smaller than that of PBI **5** (Table 1), revealing again perylene cores of **3** and **4** more rigid than

Table 1. Optical Properties of PBIs **3** and **4** and Reference **5** in Dichloromethane at Room Temperature

	λ_{max} (abs) (nm)	ε_{max} (M^{-1} cm^{-1})	λ_{max} (em) (nm)	Stokes shift (nm)	Φ_{PL} (%)
3	557	48 800	567	10	95.4
4	565	48 500	586	21	99.8
5	577	49 900	606	28	96.0

that of PBI **5**, which is indicative of smaller change of the geometry between the ground and the excited states of **3** and **4**. Both PBIs **3** and **4** show very high fluorescent quantum yields of >95%.

The perfect baseline separation of the atropo-enantiomers of PBIs **2**−**4** by HPLC (chromatogram of PBI **2** is shown in Figure S7 in Supporting Information as an example) enables accurate determination of the mole ratio of enantiomers of a PBI by intergration of the respective chromatographic peak areas. In order to determine the activation parameters for the racemization of PBI **2**, time-dependent HPLC measurements were performed at different temperatures in the range of 318−333 K (see Supporting Information). The free activation enthalpy $\Delta G^{\ddagger}_{323K}$ for the racemization process of PBI **2** was determined to be 98.5 ± 0.1 kJ mol^{-1} according to the Eyring equation, which is higher than that of the previously reported 1,6,7,12-tetrachloro-substituted PBI.[14] Table 2 collects the $\Delta G^{\ddagger}$ values for

Table 2. Free Enthalpy of Activation for the Racemization of PBIs

perylene bisimide	$\Delta G^{\ddagger}$ /kJ mol^{-1}	method
1,6,7,12-tetrachloro[a]	97.8 ± 0.1	by CD at 303 K[14]
2	98.5 ± 0.1	by HPLC at 323 K
3	99.1 ± 0.1	by HPLC at 333 K
4	98.2 ± 0.1	by HPLC at 323 K
1,6,7,12-tetraphenoxy[a]	60 ± 3	by dynamic NMR[14]

[a] For structure, see reference 14.

the racemization of PBIs with different substituents at bay area. The comparison of the $\Delta G^{\ddagger}$ values for five differently bay-substituted PBIs reveals a dependence of the free enthalpy of activation for the racemization process on the bay-area functionalization, which is quite evident in the case of PBI **4** and a previously reported 1,6,7,12-tetraphenoxy-substituted PBI.[14] The main structural difference between these two PBIs is that in the former two phenoxyl groups at one bay area are interconnected by a covalent C−C bond, which increases the free activation enthalpy of the racemization dramatically from 60 ± 3 kJ mol^{-1} (for 1,6,7,12-tetraphenoxy PBI)[14] to 98.2 ± 0.1 kJ mol^{-1} (for PBI **4**). The influence of the substituents at the other bay area on the free activation energy of racemization is rather small (compare values for PBI **2** and **4**), which indicates that indeed the 2,2′-biphenoxy linkage governs the stability of this chiral platform with regard to racemization.

In conclusion, we have shown that a simple nucleophilic substitution reaction of tetrachloroperylene bisimide with 2,2′-biphenol at one of the two bay areas affords a novel chiral PBI building block **2** with unprecedented features. PBI **2** is unsymmetric, bearing a rigid biphenoxy group at one and chlorine substituents at the other bay area. The high configurational stability imparted by the rigid 2,2′-biphenoxy bridge enabled chiral resolution of the atropo-enantiomers of this core-twisted PBI. Further functionalization of PBI **2** has been demonstrated by nucleophilic displacement of the two chlorine substituents to give PBIs **3** and **4**. The free activation enthalpies of these PBIs are sufficiently high to consider applications of these and related conjugated asymmetric platforms in chiral recognition and catalysis.

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

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