Yellow Light Emitting Highly Soluble Perylene Bisimide Dyes by Acetalization of Bay-Hydroxy Groups

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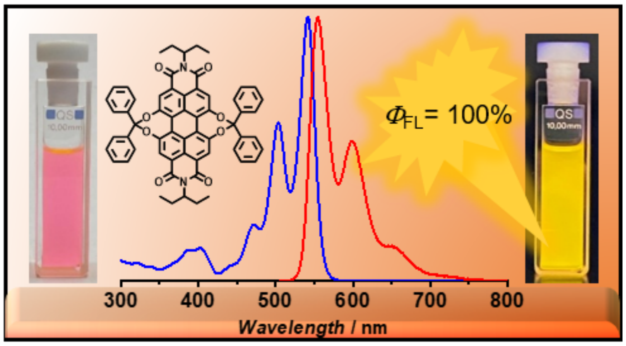
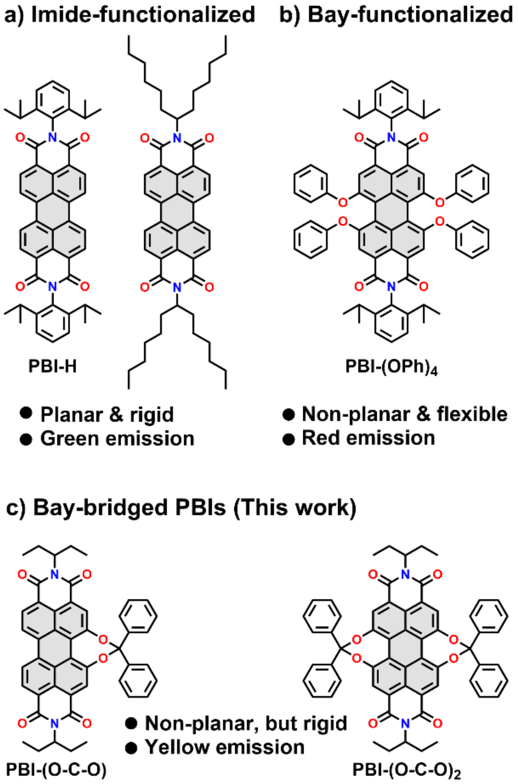


ABSTRACT: A new class of perylene bisimide (PBI) derivatives is introduced by bridging 1,12- and 1,6,7,12-hydroxy functionalized bay positions with oxygen–carbon–oxygen linker(s). This functionalization rigidifies the inherently twisted bay-substituted perylene core to afford dyes of high stability and solubility that are characterized by vibronically well-resolved absorption and fluorescence spectra and intense yellow emission with quantum yields close to 100%.

The design and synthesis of new fluorescent dyes continues to raise great interest due to the broad variety of applications ranging from light harvesting for renewable energy up to optoelectronic devices, biomolecular imaging, and optical sensing.[1,2,3,4] Most of these applications require strongly absorbing, highly fluorescent and photostable dyes. In light of this demand, perylene bisimide (PBI) dyes have attracted an enormous attention with their favorable combination of fluorescence quantum yields up to unity and outstanding photo-, thermal-, and chemical-stability originating from the electron-poor backbone, which is resistant against (photo-)oxidation.[5,6,7] Consequently, these fluorescent dyes have been successfully utilized in a wide variety of applications, including fluorescent biolabeling,[8] fluorescence analyte sensing,[9,10,11,12] electrogenerated chemiluminescence,[13] light-harvesting systems,[14,15,16] luminescent solar concentrators[17,18] as well as in light emitting devices and organic lasers[19,20,21] and the particularly demanding single molecule fluorescence spectroscopy.[22,23,24]

However, there are two critical issues with these dyes: The first is a strong propensity for aggregation and concomitant limited solubility,[5] the second is a rather narrow window of tunability of the emission wavelength. Thus, whilst the parent PBI chromophore shows superb green fluorescence with quantum yield of unity at high dilution in solution, the planar π-conjugated core is prone to aggregation, thereby leading to a reduction of the fluorescence intensity and a loss of color purity due to energy transfer from monomeric to aggregated dyes and subsequent emission of red light from excimer states.[25,26] To prevent such unfavorable property for most device applications, PBIs are commonly functionalized with bulky substituents either at the imide- or bay-positions.[7,27] The imide-substituents exert a direct effect on the aggregation of the dye by steric means. Therefore, PBI derivatives substituted with either swallow-tails (*e.g.* 1-hexylheptyl) or orthogonally-twisted aryl groups (*e.g.* 2,6-diisopropylphenyl, commercialized by BASF as Lumogen F Orange 240) at the imide-positions were developed by academic and industrial laboratories (Figure 1a).[5,6] These imide substituents efficiently prevent the aggregation of the dye, while retaining the intrinsic rigid-planar structure as well as the other favorable optical properties. Resultantly, these derivatives show vibronically well-resolved absorption and emission spectra with fluorescence quantum yields close to unity. Core substitution at bay or ortho positions, on the other hand, is not as straightforward as it exerts a pronounced effect on both structure and optical properties. Thus, controlled by the van-der-Waals radii of the respective substituents the perylene core twists and the vibronic structure is lost due to conformational heterogeneity.[28] Concomitantly larger Stokes shifts are observed. In addition, the fluorophore may not retain the favorable fluorescence properties. In this regard, in particular the functionalization with electron-donating substituents, whilst affording a desired shift of the emission to longer wavelengths, typically leads to a severe decrease of the fluorescence quantum yield.[7] In this regard, 1,6,7,12-tetraphenoxy bay-substituted derivatives **PBI-(OPh)$_4$** are exceptional (Figure 1b). Even that the absorption maximum bathochromically shifts by ca. 50 nm and fluorescence color changes to red, all favourable optical properties, namely, near unity fluorescence quantum yield, small solvent and oxygen effects, and high photostability are maintained,[29] leading to a high popularity of this fluorophore and its commercialization by BASF as Lumogen F Red 305.


a) Imide-functionalized **b) Bay-functionalized**

PBI-H

PBI-(OPh)$_4$

- Planar & rigid
- Green emission

- Non-planar & flexible
- Red emission

c) Bay-bridged PBIs (This work)

- Non-planar, but rigid
- Yellow emission

PBI-(O-C-O)

PBI-(O-C-O)$_2$

Figure 1. Molecular structures of the optically most important imide- and bay-substituted PBIs, and the bay-bridged derivatives reported in this work.

Accordingly, among PBI emitters, the molecular structures shown in Figure 1a,b are the most popular ones, being well soluble and providing either green (**PBI-H**) or red (**PBI-(OPh)$_4$**) fluorescence with high fluorescence quantum yields. Here, we introduce two new PBI-derivatives shown in Figure 1c that exhibit similarly good solubility, little propensity for aggregation and intense fluorescence of yellow light. As we will show, these dyes are readily accessible from the corresponding 1,12-dihydroxy and 1,6,7,12-tetrahydroxy precursors via acetalization of their hydroxy bay-substituents with carbon bridge(s). These derivatives exhibit a non-planar π-scaffold, but still possess the desired rigidity, leading to photo-physical properties comparable to those of the most valued PBI derivatives, green emitting **PBI-H** or red emitting **PBI-(OPh)$_4$**.

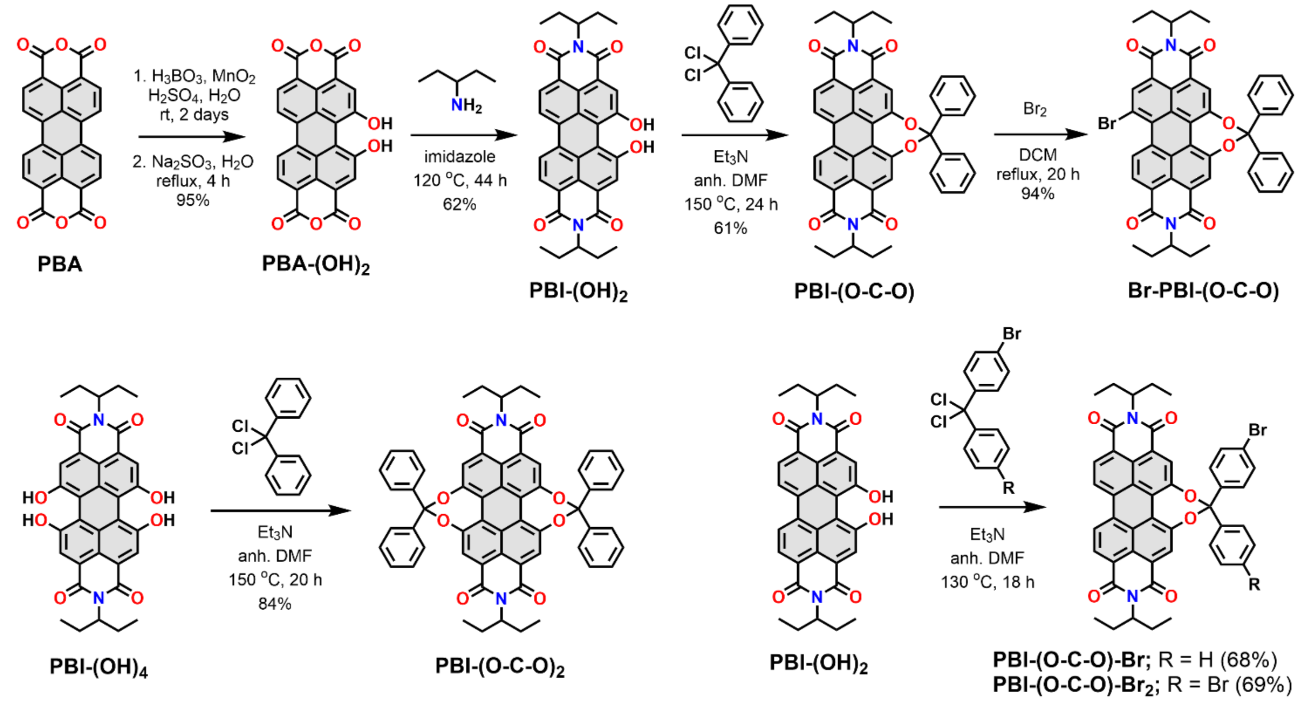
The syntheses of the two bay-bridged target molecules, **PBI-(O-C-O)** and **PBI-(O-C-O)$_2$**, have been achieved from 1,12-dihydroxy- and 1,6,7,12-tetrahydroxy-PBIs as the precursor molecules, respectively (Scheme 1). For the synthesis of singly bay-bridged **PBI-(O-C-O)**, parent perylene bisanhydride (**PBA**) has been used as the starting compound. At first, **PBA** was oxidized with activated MnO_2 to obtain 1,12-dihydroxy-PBA (**PBA-(OH)$_2$**) in high yield (95%) using the protocol previously described by Schill *et al* for the oxidation of perylene bisimides.[30] Herein, by the synthesis of **PBA-(OH)$_2$**, we have made this protocol widely applicable as various 1,12-dihydroxy-PBI derivatives can be easily obtained in just one-step using **PBA-(OH)$_2$** as a precursor. Subsequent imidization of **PBA-(OH)$_2$** with 3-aminopentane gave the corresponding 1,12-dihydroxy-PBI (**PBI-(OH)$_2$**), which was reacted with diphenyldichloromethane in presence of a base to receive the singly bay-bridged compound **PBI-(O-C-O)** in a good yield of 61%. Following the same reaction, the doubly bay-bridged derivative **PBI-(O-C-O)$_2$** has been achieved in even higher yield of 84% from 1,6,7,12-tetrahydroxy-PBI (**PBI-(OH)$_4$**), which was synthesized following the procedure developed in our group before.[31,32] These bay-bridged derivatives exhibit excellent solubility in common organic solvents at room temperature despite of the presence of a relatively small 3-pentyl group at the imide positions (Table S1). Remarkably, their solubility in chloroform (75 mg/mL for **PBI-(O-C-O)** and 93 mg/mL for **PBI-(O-C-O)$_2$**) is significantly higher compared to that of imide-substituted **PBI-H** (5 mg/mL), which clearly demonstrates the efficacy of bridge-moiety to prevent the aggregation. Also, these derivatives are highly stable towards light and air as a solid and in solutions, showing no signs of decomposition after storage in ambient conditions for several months.

This newly developed synthetic protocol has a high scope for further derivatization. As an example, monobromination of singly bay-bridged **PBI-(O-C-O)** gave corresponding 6-bromo-substituted derivative **Br-PBI-(O-C-O)** in 94% yield (Scheme 1), which opens the ways for further functionalization of perylene core and tuning of the properties. Similarly, functionalization of the carbon bridge is also possible simply by using bromo-substituted diphenyldichloromethane derivatives as proved by the facile synthesis of compounds **PBI-(O-C-O)-Br** and **PBI-(O-C-O)-Br$_2$** (Scheme 1). These derivatives are of especial importance as they not only allow an extension of the bridge, but also provide the option for the attachment of functional moieties to the bridge without changing the inherent optical properties of the perylene bisimide core.

To elucidate the effect of the bay substituents on the molecular structure, single crystals suitable for X-ray analysis were grown for a 1,12-dihydroxy-PBI derivative (**PBI-(OH)$_2$-Cy**, *N*,*N′*-dicyclohexyl-1,12-dihydroxyperylene bisimide, Figure S1) and for the two bay-bridged PBIs, **PBI-(O-C-O)** and **PBI-(O-C-O)$_2$**. Compound **PBI-(OH)$_2$-Cy**, crystallized in the *P*-1 space group, illustrates the twisting of the chromophore's π-core introduced by the two hydroxyl groups (Figure S1). The dihedral angle of the unsubstituted bay area $\sphericalangle$ (C_6–C_{6a}–C_{6b}–C_7) is 13.2°, whereas the angle of the hydroxylated bay area $\sphericalangle$ (C_1–C_{12b}–C_{12a}–C_{12}) is 26.2°. This is in good accordance with previous observations on 1,6,7,12-tetramethoxy-PBIs with twist angles between 26° and 30° for the substituted sides.[31,33] The value is at the lower limit, which can be attributed to the formation of an *intra*molecular hydrogen bond between the two neighbouring hydroxy groups at 1- and 12-positions with a distance of 2.55 Å between the two oxygens, forming a seven-membered ring. The second OH-proton forms in the solid-state an *inter*molecular hydrogen bond to the carbonyl group of a neighbouring PBI with a slightly larger O-O distance of 2.69 Å.

The compounds **PBI-(O-C-O)** and **PBI-(O-C-O)$_2$** crystallized in the $P2_{1/n}$ and the *P*-1 space groups, respectively. The crystal structure of the singly-bridged-compound **PBI-(O-C-O)** exhibited a dihedral angle of 7.6° for the unsubstituted side ($\sphericalangle$ (C_6–C_{6a}–C_{6b}–C_7)) and of 8.6° for the substituted side ($\sphericalangle$ (C_1–C_{12b}–C_{12a}–C_{12})) of the molecule (Figure 2). This sharp decrease of

Scheme 1. Synthesis of singly and doubly bay-bridged perylene bisimides, **PBI-(O-C-O)** and **PBI-(O-C-O)$_2$**, and brominated derivatives of **PBI-(O-C-O)**.



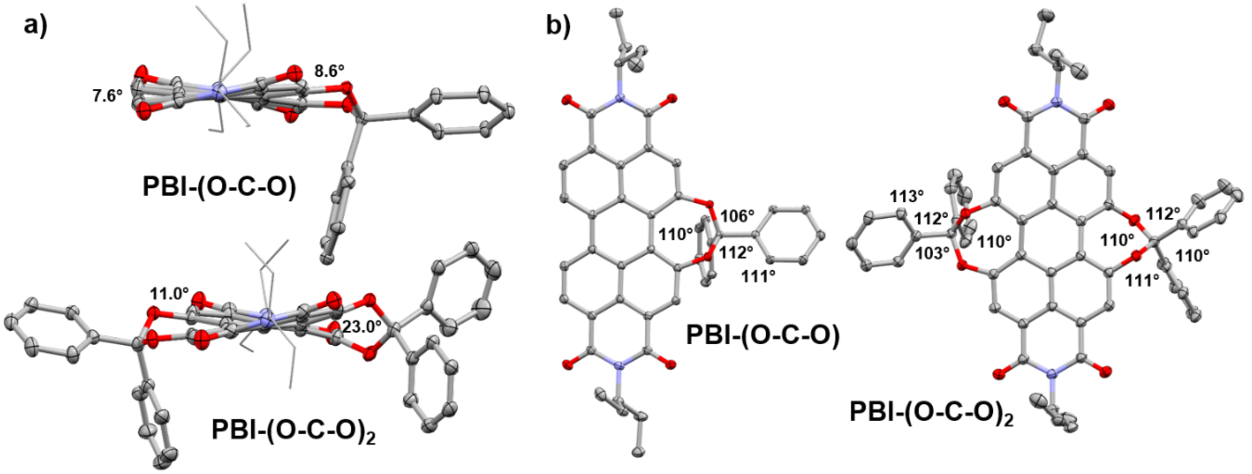


Figure 2. Molecular structures of **PBI-(O-C-O)** and **PBI-(O-C-O)$_2$** according to single crystal X-ray analyses: a) view along the *N,N′* axis with twist angles of bay-region of perylene core and b) top view with relevant bond angles. Ellipsoids are set to 50% probability. Hydrogen atoms, disorder as well as solvent molecules are excluded for clarity.

dihedral angles as compared to 1,12-dihydroxy-PBI (13.2 and 26.2°, respectively) clearly illustrates the rigidification of the perylene core as an effect of bay-bridging. For the doubly bridged **PBI-(O-C-O)$_2$**, also two different dihedral angles can be found. One side is twisted with 11.0°, whereas the other side shows more than the doubled value with 23.0°. It is noteworthy that this compound has a less twisted perylene core as compared to the tetraphenoxy-substituted PBIs that have a dihedral angle in the range of 25–33°, an effect that can again be attributed to the bridging of the bay-positions.[34,35,36] The O-C-O angles of the seven-membered ring for singly- and doubly-bridged PBIs (ca. 110°) are in good accordance with the literature, which is also the case for the C-O bonds in the seven-membered ring with values of 1.42 Å.[37] Further angles of the bridging unit can be seen in Figure 2.

The optical properties of bay-bridged PBIs were investigated by UV-vis absorption and fluorescence spectroscopy in toluene, chloroform, and THF. The obtained results were compared with 2,6-diisopropylphenyl-substituted **PBI-H** and tetraphenoxy-bay-substituted **PBI-(OPh)$_4$** to evaluate the changes in optical properties induced by the bridging of bay-region (Figure 3 and Table S2). Interestingly, in contrast to other bay-substituted and accordingly twisted PBIs (e.g. **PBI-(OPh)$_4$**), the bay-bridged PBIs **PBI-(O-C-O)** and **PBI-(O-C-O)$_2$** show spectra with well-resolved vibronic progressions for their intense S$_0$–S$_1$ transitions, comparable to those observed for planar imide-substituted PBIs (e.g. **PBI-H**). This indicates a rather minor geometry change upon optical excitation, presumably, due to the locked seven-membered ring(s) in the bay-area(s). Notably, both bridged derivatives exhibited almost identical absorption spectra, except a minor difference in the S$_0$–S$_2$ transition for which the maximum shifted from 402 nm for singly-bridged to 418 nm for doubly-bridged derivative. These compounds displayed absorption maxima at 542 nm, which is bathochromically shifted as compared to **PBI-H** (λ_{max} = 527 nm) but hypsochromically shifted compared to **PBI-(OPh)$_4$** (λ_{max} = 576 nm). Similarly, the molar extinction coefficients of these compounds in chloroform (ca. 64000 M^{-1}cm^{-1}) are lower than those of **PBI-H** (94000 M^{-1}cm^{-1}), but higher than those of **PBI-(OPh)$_4$** (50000 M^{-1}cm^{-1}).

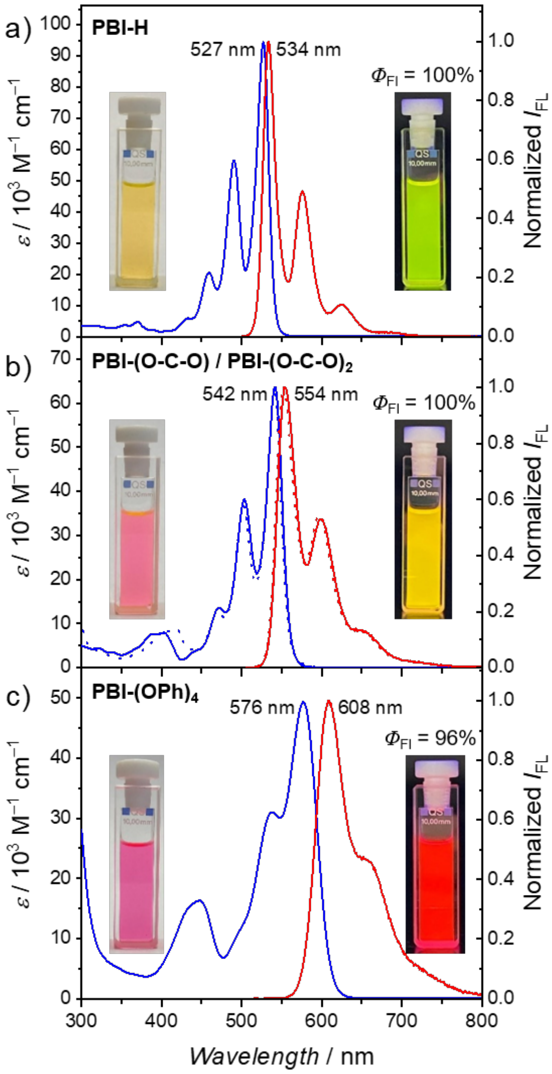


Figure 3. Absorption (blue lines, c = 20 μM) and fluorescence (red lines) spectra of a) **PBI-H**, b) **PBI-(O-C-O)** (solid lines) and **PBI-(O-C-O)$_2$** (dashed lines), c) **PBI-(OPh)$_4$** in chloroform at 295 K. Insets: Photographs of chloroform solutions of compounds under visible light (left) and under UV light (right).

Like for the absorption spectra, the bridged molecules also showed fluorescence spectra characteristic for rigid PBIs with their maxima centered at 554 nm and well-resolved vibronic fine structure with mirror-image relation to the absorption band. Here as well, the spectra are bathochromically sifted as compared to **PBI-H** (λ_{em} = 534 nm) but hypsochromically shifted compared to **PBI-(OPh)$_4$** (λ_{em} = 608 nm). This shift explains their distinct yellow fluorescence as compared to green emission of **PBI-H** and red emission of **PBI-(OPh)$_4$**. Notably, both compounds have significantly smaller Stokes shifts of 400 cm^{-1} in comparison to **PBI-(OPh)$_4$** (910 cm^{-1}) that further corroborates the higher rigidity of the perylene core for these compounds. Furthermore, these compounds exhibit fluorescence quantum yields of almost unity and long fluorescence lifetimes of 5.2–5.5 ns with mono-exponential decays even in the presence of atmospheric oxygen. These values are well in line with **PBI-H** with 3.7 ns and **PBI-(OPh)$_4$** with 6.0 ns.[38] Owing to higher molar extinction coefficients of these bridged molecules as compared to **PBI-(OPh)$_4$**, their optical brightness ($\varepsilon_{max}\cdot\Phi_{fl}$) values >60000 M^{-1}cm^{-1} surpass that of **PBI-(OPh)$_4$** (48000). This makes the bridged molecules attractive for their application as fluorescent emitters in bioimaging and light harvesting in luminescent solar light concentrators. Like for **PBI-H** and **PBI-(OPh)$_4$** the absorption and fluorescence properties of the new dyes **PBI-(O-C-O)** and **PBI-(O-C-O)$_2$** are little affected by the solvent (Table S2).

In conclusion, a new synthetic strategy has been devised that rigidifies the twisted with hydroxy groups bay-substituted perylene bisimide (PBI) derivatives in a facile manner by acetal bridging units. The most prominent feature of resultant bay-bridged compounds is their superb optical properties, which resemble more to the planar parent PBIs as compared to the non-planar bay-substituted PBIs as a result of the rigidity induced by bay-bridging. Consequently, vibronic fine-structure has been observed, wherein the fluorescence spectra displayed mirror image relationship with the absorption spectra and a significantly smaller Stokes shift as compared to 1,6,7,12-tetraphenoxy-PBIs. These bay-bridged derivatives are strong yellow emitters with almost unity fluorescence quantum yields and lifetimes >5 ns. Most importantly, the optical properties are robust and remain invariable to the external environment, such as solvent polarity and the presence of oxygen. This makes these yellow emitters promising candidates for all those applications, from single-molecule spectroscopy to optical sensing to luminescent solar concentrators, for which the green light emitting parent PBIs and the red light emitting 1,6,7,12-tetraphenoxy-PBIs have been successfully utilized so far. All in all, this work opens the way to a new class of perylene bisimide-based functional materials whose properties are hybrid to those of planar imide-substituted PBIs and non-planar bay-substituted PBIs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details, spectroscopic data, crystallographic data, electrochemical analysis (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

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