

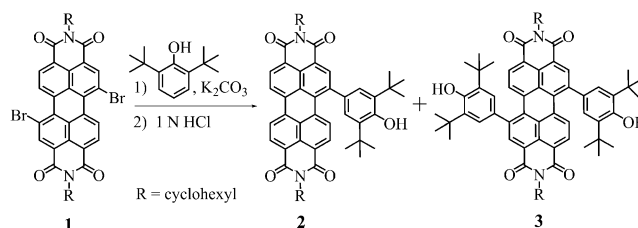
Halochromic Phenolate Perylene Bisimides with Unprecedented NIR Spectroscopic Properties

Mei-Jin Lin, Benjamin Fimmel, Krzysztof Radacki, and Frank Würthner*

Organic π -conjugated dyes with strong absorptions in the near-infrared (NIR) region have received increasing attention in the past decades owing to their highly interesting but less studied electrical/optical properties and foreseeable applications in NIR light-emitting diodes,^[1] biosensing,^[2] photovoltaic cells,^[3] and telecommunication.^[4] The most prevalent organic dyes such as cyanines,^[5] squaraines,^[6] Bodipys,^[7] porphyrins,^[8] phthalocyanines,^[9] and rylene^[10] are absorbing in the visible region of light, and common strategies to achieve a bathochromic shift of the absorption maximum of a dye are the incorporation of donor and acceptor groups into the parent chromophore and the extension of the π system of the chromophore.^[11] The introduction of both donor and acceptor substituents into the parent chromophore leads to charge transfer (CT) bands in the long-wavelength region of the absorption spectrum, which is a simple but promising strategy to achieve long-wavelength absorbing dyes. On the other hand, the extension of the π system of the chromophore is more elaborate and is often accompanied by decreased chemical stability, for example, for cyanine and squaraine dyes, or poor solubility, for example, for porphyrin, phthalocyanine, and rylene bisimide dyes, thus limiting their scope for applications.

Perylene bisimides (PBIs) are an attractive class of electron-poor dyes owing to their outstanding optical, electronic (n-type semiconducting), and light fastness properties.^[12] Owing to the electron-deficient character of the PBI core, the latter can be considered as an electron-accepting moiety that may interact with strong electron-donating functional groups attached to it and thus give rise to CT bands.^[13] So far, only few examples of PBIs bearing strong electron-donor substituents such as 4-(diphenylamino)phenyl, [4-(diphenylamino)phenyl]ethynyl, and oligothiophene-based moieties at the bay area showed the spectral features that are characteristic of charge transfer, but their absorption maxima remained below 800 nm.^[13,14] Molecular orbital calculations indicated that the highest occupied molecular orbitals (HOMOs) of such PBIs are mainly

localized on the donor substituents, while the lowest unoccupied molecular orbitals (LUMOs) are similar to those of core-unsubstituted parent PBIs.^[14] Thus, an increase of the donor strength of substituents is expected to result in PBI derivatives with a strong bathochromic shift of their CT bands. Analysis of Hammett coefficients^[15] suggests that a more pronounced electron-donating effect can be anticipated upon replacement of the amino groups ($\sigma_p^+ = -1.4$ for $-NPh_2$), which were previously applied to PBIs,^[13,14] by an oxide anion ($\sigma_p^+ = -4.27$ for $-O^-$) to achieve strongly bathochromically shifted absorptions of PBIs. Herein, we report that this concept is indeed viable. For the realization of this concept, we have synthesized a pair of novel halochromic 4-hydroxyphenyl-substituted PBIs **2** and **3** (Scheme 1), the anions of which exhibit so far unprecedented NIR absorptions for PBI dyes beyond 1100 nm because of the exceptionally strong electron-donating oxide anion introduced into the phenyl substituent at the *para* position.



Scheme 1. Synthesis of 4-hydroxyphenyl-substituted PBIs **2** and **3**. Reaction conditions and yields are given in Table 1.

Table 1: Reaction conditions and yields of the isolated products PBIs **2** and **3**.

Entry	Solvent	T [°C]	t [h]	Yield of 2 [%] ^[a]	Yield of 3 [%] ^[a]
1	DMF ^[b]	80	3	38	0
2	DMF	80	48	31	0
3	DMF	120	3	41	0
4	NMP ^[c]	120	3	57	8.1
5	DMSO ^[d]	120	3	53	12

[a] The yield is referred to the starting material 1,7-dibrominated PBI **1**;

[b] DMF: dimethylformamide; [c] NMP: *N*-methylpyrrolidin-2-one;

[d] DMSO: dimethyl sulfoxide.

Unlike the known PBIs that are aryl-substituted at the bay area, which were usually prepared by transition-metal catalysis,^[12c] the present PBIs **2** and **3** bearing one or two 4-hydroxyl-3,5-di-*tert*-butylphenyl units at the bay area, respectively, are synthesized by nucleophilic substitution of 1,7-dibrominated PBI **1**^[16] with excess amounts of the nucleophile

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2,6-di-*tert*-butylphenolate ion,^[17] followed by protonation with acid (Scheme 1). To our surprise, no matter which reaction conditions we applied (see Table 1), the hydrodebrominated mono(4-hydroxyphenyl)-substituted PBI **2** was obtained as the major product in 31–57% yield. However, a small amount of di(4-hydroxyphenyl)-substituted PBI **3** (8.1–12% yield) could be obtained when *N*-methylpyrrolidin-2-one (NMP) or dimethyl sulfoxide (DMSO) was used as a reaction solvent.

Mechanistically, a $S_{RN}1$ -type reaction sequence (see Scheme S1 in the Supporting Information) may account for the observed products.^[18] Owing to the electron-deficient character of the PBI core, the 1,7-dibrominated PBI **1** may accept an electron from the phenolate ion, thus forming a PBI radical anion, which after elimination of a bromide ion either abstracts a proton from the medium to form monobrominated PBI, or is substituted by the 2,6-di-*tert*-butylphenolate ion to generate a monobromo-mono(4-hydroxy-phenyl)-substituted PBI radical anion. The latter species may undergo another debromination step and subsequently either react with the phenolate ion to generate the radical anion of di(4-hydroxy-phenyl)-substituted PBI **3**, or may abstract a proton to form mono(4-hydroxyphenyl)-substituted PBI **2** (for details, see the Supporting Information). Evidence for the formation of PBI radical anions is given by a color change of the solution from red to green during the reaction, which is in accordance with the spectral characteristics of spectroelectrochemically generated PBI radical anions.^[19] A certain amount of the oxidation product 3,3',5,5'-tetra-*tert*-butyl-4,4'-dibenzoquinone (for ^1H and ^{13}C NMR spectra, see Figure S3–S4 in the Supporting Information) of 2,6-di-*tert*-butylphenoxide radicals and core-unsubstituted PBI (the latter is formed by debromination of PBI **1**) were detected under the various reaction conditions applied, which strongly supports the proposed $S_{RN}1$ mechanism for the formation of 4-hydroxyphenyl-substituted PBIs **2** and **3**. Moreover, the fact that the highest yield (12%) of di(4-hydroxyphenyl)-substituted PBI **3** was obtained in DMSO, which is an ideal solvent for $S_{RN}1$ reactions owing to its low reactivity as a hydrogen-atom donor towards aryl radicals,^[20] corroborates such a radical mechanism.

The molecular structures of PBIs **2** and **3** were assigned by 1D and 2D NMR spectroscopy (see Figure S5–S8) as well as by single-crystal X-ray analyses (for details and crystal data, see the Supporting Information), which unequivocally confirm their structures with a C–C coupling between the perylene core and the functional 4-hydroxy-3,5-di-*tert*-butylphenyl unit (Figure 1). In the crystal of PBI **2**, two pairs of

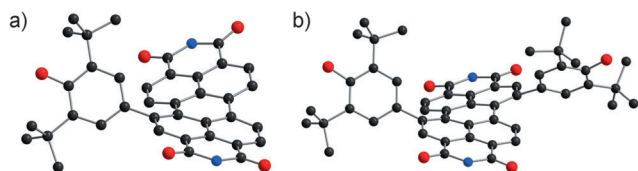


Figure 1. Molecular structures of a) PBI **2** and b) PBI **3** determined by X-ray analysis: red, blue, and black balls represent O, N, and C atoms, respectively. For clarity, the hydrogen atoms and cyclohexyl groups were omitted.

enantiomers (*P* and *M* atropo-enantiomers)^[21] with the twist angles between the two naphthalene units being 18.9° and 19.2°, respectively, are found. The chiral self-recognition of these enantiomers by π – π stacking in the solid state led to (*P,P*) and (*M,M*) homochiral dimers,^[22] which are further self-discriminated by H-bonding interactions between the OH donor in the phenol and the C=O acceptor in the imide units to form a racemic 1D network with an alternate *P* and *M* chirality (see Figure S1a). From the ^1H NMR spectra of PBI **2** in CD_2Cl_2 at different concentrations (10^{-5} – 10^{-2} M), a slight tendency for aggregation by π – π stacking is noticeable at higher concentration (10^{-2} M; see Figure S9). Thus, in order to avoid aggregation, the spectroscopic properties of PBIs **2** and **3** have been studied in dilute solutions (10^{-5} M).

Despite two bulky 4-hydroxy-3,5-di-*tert*-butylphenyl groups at both bay areas, PBI **3** exhibits a less twisted perylene core (about 16.7°) than that of the monosubstituted PBI **2**. As expected, no π – π stacking of perylene cores is observed in the crystal of PBI **3** (see Figure S1b). In accordance with the X-ray analysis, no indication for π – π aggregation could be found in the ^1H NMR spectra of PBI **3**, not even for a highly concentrated solution (10^{-2} M; see Figure S10).

The optical properties of the neutral PBIs **2** and **3** in dichloromethane (DCM) were explored by UV/Vis absorption and fluorescence spectroscopy (see Figure 2). At room

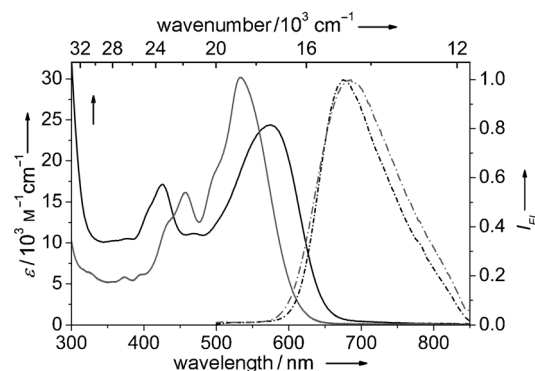


Figure 2. UV/Vis absorption (solid lines) and normalized emission spectra ($\lambda_{\text{ex}} = 450$ nm, dashed-dotted lines) of PBIs **2** (gray) and **3** (black) in dichloromethane at room temperature.

temperature, the UV/Vis spectra of PBIs **2** and **3** showed absorption maxima at 534 nm (18726 cm^{-1}) and 578 nm (17301 cm^{-1}), respectively, which are shifted bathochromically by 249 cm^{-1} and 1674 cm^{-1} with respect to that of the parent PBI without bay substituents (absorption maximum at ca. $527\text{ nm}^{[12]}$). The most remarkable feature of the absorption spectra is, however, the loss of vibronic fine structure for both PBIs **2** and **3** and the very intensive absorption throughout the whole visible range for PBI **3**. The UV/Vis spectra in solvents of different polarity show quite similar absorption maxima (Table S1) and spectral shapes (Figure S11). Accordingly, the absorption properties are not governed by a significant charge transfer from the 4-hydroxyphenyl substituents to the PBI core but are more likely to be caused by the distortion of the

aromatic system evoked by sterical congestion in the bay area. Similar conclusions can be drawn from the fluorescence spectra of PBIs **2** and **3** that exhibit broad emission bands with large Stokes shifts at 675 and 685 nm, and fluorescence quantum yields of only 4.2% and 2.4%, respectively.

Phenol is a well-known halochromic unit in common pH indicators such as phenol red, thymol blue, and Reichardt betaines.^[23] As expected, upon addition of organic base tetrabutylammonium hydroxide (TBAH) to a dichloromethane solution of PBI **2**, the color of the solution changes. While the color change from red to orange appears modest (Figure 3a, inset), UV/Vis-NIR spectroscopy reveals that the major effect of TBAH addition is not the change in the visible

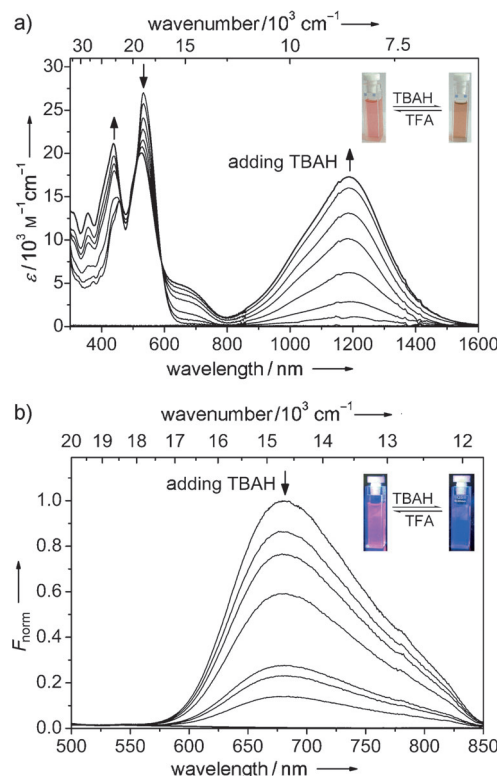


Figure 3. UV/Vis absorption (a) and emission (b, $\lambda_{\text{ex}} = 450$ nm) spectral changes of PBI **2** in dichloromethane (10^{-5} M) with increasing amounts of TBAH ((0.0, 0.5, 1.0, 1.5, 2.0, 6.0, 20, 30) $\times 10^{-5}$ M). The insets show the color changes in absorption (a) and fluorescence upon excitation with a UV lamp (b) of PBI **2** in dichloromethane.

spectral range (decrease of the band at 534 nm accompanied by a slightly hypsochromic shift to 528 nm and an increase of the band at 457 nm accompanied by a slightly hypsochromic shift to 439 nm) but the appearance of an entirely new band in the NIR region with an absorption maximum at 1179 nm (8481 cm^{-1} ; Figure 3a). Almost the same spectral changes are observed for PBI **3** upon addition of TBAH (Figure S12a). For both PBIs **2** and **3**, spectral changes similar to those in dichloromethane are observed in other solvents such as DMSO and nitrobenzene (see Figure S13).

These spectral features are obviously related to the deprotonation of the phenol substituents in PBIs **2** and **3** by

TBAH base to give the respective phenolate-substituted anionic PBIs **2**[−] and **3**^{2−}, the formation of which could indeed be substantiated by ^1H NMR spectroscopy (see Figure S14a and S15a). Accordingly, the unprecedented absorption bands in the NIR region at 1179 nm for the PBI **2**[−] anion ($\Delta\tilde{\nu} = 10494 \text{ cm}^{-1}$ compared to that of the bay-unsubstituted parent PBI^[12]) and 1185 nm for PBI **3**^{2−} ion in dichloromethane are attributed to a pronounced charge transfer from the electron-rich phenolate bay substituents to the electron-poor PBI, which is supported by molecular orbital calculations (see the Supporting Information). Although CT bands were previously observed for PBIs bearing 4-(diphenylamino)phenyl and [4-(diphenylamino)-phenyl]ethynyl substituents at the bay positions, the bathochromic shifts in those cases are only modest and could not attain the highly desirable NIR spectral range, that is, their absorption maxima are at 653 nm^[13a] and 718 nm,^[14b] respectively. The formation of PBI **2**[−] and **3**^{2−} ions could also be followed by fluorescence spectroscopy as the fluorescence intensities of PBI **2** and PBI **3** in DCM decrease gradually with an increase in concentration of TBAH (Figure 3b and Figure S12b).

The color, UV/Vis-NIR, and fluorescence spectra of neutral PBIs **2** and **3** could be recovered by addition of trifluoroacetic acid (TFA) to solutions of PBIs **2** and **3** in dichloromethane containing TBAH, hence confirming the reversible nature of the deprotonation/reprotonation process (see Figure S14 and S15). This reversible behavior has also been confirmed by the ^1H NMR spectra showing that all the proton signals, except those for the alkyl groups, changed upon addition of TBAH to solutions of PBIs **2** and **3** in deuterated dichloromethane, and that their initial spectra are recovered after the addition of TFA to the TBAH-containing solutions (see Figure S14 and S15).

In conclusion, we have discovered a facile synthetic pathway for novel halochromic 4-hydroxyphenyl-substituted PBIs. To the best of our knowledge, such a synthetic pathway for C–C coupling without transition-metal catalysis in the bay area of perylene bisimide dyes is unprecedented. More importantly, the anions of the hitherto unknown halochromic 4-hydroxyphenyl-functionalized PBIs exhibit NIR absorptions close to 1200 nm, which were so far elusive for the perylene dye family. Thus, further studies on this unique class of halochromic PBIs in various directions are well motivated.

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