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Zwitterionic Radicals

Ambient Stable Zwitterionic Perylene Bisimide-Centered Radical

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Dedicated to Professor Franz Effenberger on the occasion of his 85th birthday

***Abstract:** The unexpected introduction of a cationic imidazolium substituent in the 2-position of a tetrachloro-substituted perylene-3,4:9,10-tetracarboxylic acid bisimide (PBI) by the reaction of PBI-Cl_4 **1** with the N-heterocyclic carbene 1,3-di-iso-propyl-imidazolin-2-ylidene (^{i}Pr_2Im **2**) enables the isolation of an ambient stable zwitterionic radical. The remarkable stability of this unprecedented PBI-centered radical facilitates the complete characterization by several spectroscopic methods as well as single crystal structure analysis. Redox studies revealed that ^{i}Pr_2Im-PBI-Cl_4 **4** can be transferred reversibly to the corresponding anion and cation, respectively, even on a preparative scale.*

Perylene-3,4:9,10-tetracarboxylic acid bisimides (PBIs) are an outstanding class of organic dye molecules that have been utilized since more than half of a century as industrial pigments.[1] Even earlier this class of compounds has been applied as red colorants in the industrial vat dyeing process, in which water-insoluble PBIs are reduced to the corresponding water-soluble PBI anions (leuko compounds).[2] More recently, owing to the n-type semiconducting properties, the interest in these multifunctional organic molecules has grown tremendously in the research fields of organic electronics and photovoltaics.[3] The success of PBIs in these applications is attributed to the ease of reduction into rather stable and delocalized radical anions that is a common feature of electron-deficient aromatic diimides.[4] Accordingly, the formation of PBI radical anions has been addressed intensively to improve (semi)conductive properties, leading to outstanding air-stable n-channel transistors,[3] as well as n-type interfacial layers, conducting nanobelts, and photoconductive films.[5] Nevertheless, most of the studies described in the literature are concerned with the chemical, electrochemical, or photochemical reduction of neutral PBIs to anionic PBI species that will be reoxidized upon exposure to air. Even though these reduced species were unambiguously identified by UV/Vis-NIR absorption and EPR spectroscopy as well as theoretical considerations, the amount of in situ-generated PBI anions can only be estimated.[5b,6] Surprisingly, despite these interesting and fundamental investigations, the isolation and complete characterization of an ambient stable PBI radical anion and/or PBI dianion still remains an unsolved scientific challenge. In this contribution we communicate the first example of a facile straightforward synthesis of an ambient stable zwitterionic PBI-centered radical that was fully characterized by single-crystal X-ray analysis. According to our studies this organic radical can be interpreted as a PBI radical anion that is stabilized by a σ-bonded imidazolium cation.

As the introduction of electron-withdrawing groups (EWGs) in the *ortho*- and/or bay-position will shift the reduction potential of PBIs to more positive values and thus increase the electron affinity, we became interested in a new class of PBI molecules that are equipped with cationic bay substituents as alternatives for the common EWGs like -F, -Cl, -Br, -CN, or -CF_3.[6h,7] With this basic concept in mind we thought to replace the four chlorine atoms of *N,N'*-dibutyl-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic acid bisimide (PBI-Cl_4 **1**) with the highly nucleophilic N-heterocyclic carbene 1,3-di-*iso*-propyl-imidazolin-2-ylidene (^{i}Pr_2Im **2**) to generate extremely electron-deficient PBI-substituted imidazolium chlorides. Immediately after adding four equivalents of ^{i}Pr_2Im to a suspension of PBI-Cl_4 in dry toluene a color change from orange to green occurred that was followed by the formation of a viscous green precipitate. To our surprise, after recrystallization of the isolated solid from a saturated acetone solution, the product could be identified as the zwitterionic PBI-centered radical ^{i}Pr_2Im-PBI-Cl_4 **4**, in which the cationic imidazolium substituent has been introduced in the *ortho*-position to the imide functionality (Scheme 1). An alternative purification, for example, by column chromatography, seems not to be feasible due to oxidation on silica as well as in different organic solvents like dichloromethane (Figure S1). In this context it has to be mentioned that **4** can also be prepared by reacting equimolar amounts of **1** and **2**, however, in a significantly lower yield (10%).

Due to the paramagnetic nature of **4**, only strongly broadened resonances between 0.50 and 3.50 ppm were detected by proton NMR spectroscopy that cannot be further interpreted (Figure S2). However, the zwitterionic radical was unequivocally characterized by UV/Vis absorption and EPR spectroscopy as well as high-resolution mass spectrometry and elemental analysis (see below). Single crystals of **4** were grown from a saturated acetone solution at room temperature to unambiguously determine the structure and the connectivity of this exceptional molecule (Figure 1). ^{i}Pr_2Im-PBI-Cl_4 **4** builds up a one dimensional stack that is characterized by alternating π–π distances (3.61 and 4.74 Å, Figure 1) in contrast to the equidistant stacking mode (3.64 Å, Figure S3) that was found for the neutral PBI-Cl_4 **1** by single-

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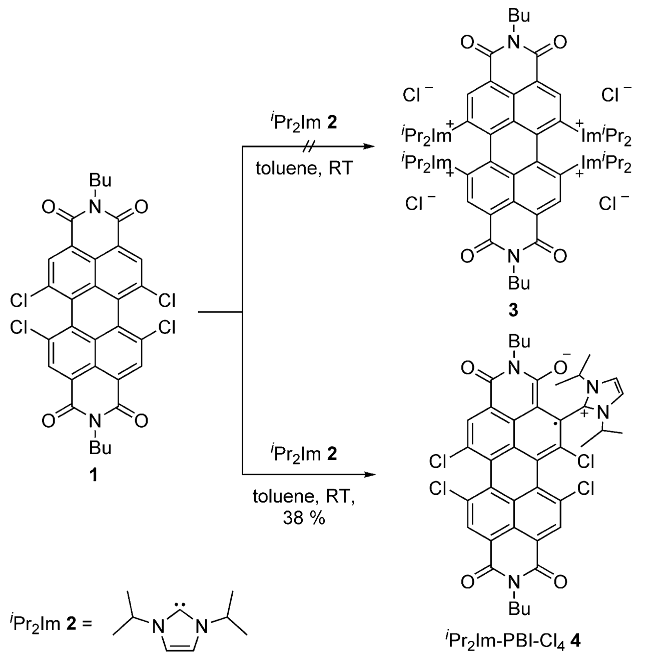


Scheme 1. Reaction of PBI-Cl$_4$ **1** with ^{i}Pr$_2$Im **2** under formation of the zwitterionic PBI-centered radical ^{i}Pr$_2$Im-PBI-Cl$_4$ **4**.

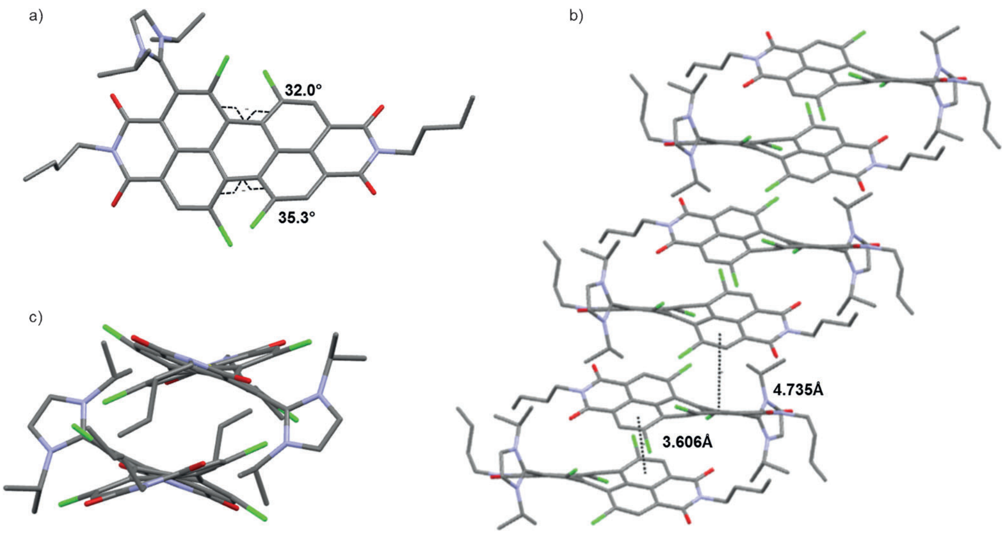


Figure 1. Molecular structure of ^{i}Pr$_2$Im-PBI-Cl$_4$ **4** in the solid state. Hydrogen atoms have been omitted for clarity. a) Top view on the PBI surface. b) One-dimensional stack along the *a*-axis. c) View along the long axis of a PBI dimer.

crystal X-ray diffractometry. The plane of the cationic imidazolium substituent at the 2-position is twisted 75.1° out of the PBI mean plane as a result of steric repulsion between the bulky *iso*-propyl groups and the oxygen and chlorine atoms. Furthermore, the asymmetric substitution pattern of **4** leads to an unequal twist in the bay areas of the PBI core (32.0° and 35.3°). Comparing the average bond lengths of zwitterionic **4** with parent PBI **1**, minor deviations concerning all peripheral C–C bonds of the aromatic core, the two C–C bonds joining the naphthalene monoimide subunits, and the four C=O bonds can be ascertained (Figure S4 and Table S1 highlighted in red), whereas the inner carbon skeleton of the PBI reveals no significant alterations (Figure S4 and Table S1 highlighted in blue). These very small changes are in line with theoretical considerations by Rybtchinski et al. who calculated the bond lengths of PBI-centered radical anions to be intermediate between neutral PBIs and the corresponding PBI dianions.[6f] According to these investigations the affected C–C bonds (peripheral ones) should reveal alternating bond distances as it can be recognized for **4**. Furthermore, as some of the additional electron density is delocalized into the C=O π* orbitals, a slight elongation (~0.010 Å) of these bonds is observed accompanied with a reduced C=O stretching vibration as it has been confirmed by IR spectroscopy (Figures S5–S7). Thus, whereas an intensive C=O stretching vibration can be detected at 1697 cm^{-1} for the neutral PBI-Cl$_4$ **1**, the corresponding C=O vibration of **4** is significantly shifted to lower wave numbers (1664 cm^{-1}).

The optical properties of **4** were investigated by UV/Vis absorption spectroscopy in different solvents (Figure 2, top and Figure S8) as well as in acetone at different concentrations (Figure S8) and by spectroelectrochemistry (Figure S9). In good agreement with the values reported for electrochemically generated PBI radical anions, three intensive absorption bands at 752, 928, and 1035 nm were observed for PBI zwitterion **4** that are concentration- as well as solvent-independent.[4,6a] These data are consistent with the results obtained by spectroelectrochemistry upon electrochemical reduction of **1** to the radical anion, for which three new absorption bands, analogous to the characteristic ones of **4**, increase within the NIR-region at 756, 918, and 1013 nm at potentials of −350 to −600 mV (Figure 2, top and Figure S9). Applying a lower potential leads to a decrease of these absorption bands accompanied by an increase of the shorter-wavelength absorption at 680 nm that can be assigned to the PBI-Cl$_4^{2-}$ dianion. Interestingly, similar absorption bands can be generated from **4** upon oxidation and reduction. However, due to the cationic imidazolium substituent all absorption bands of **4** with exception of the one at 752 nm are bathochromically shifted. The introduction of the electron-withdrawing imidazolium substituent at the 2-position significantly shifts the redox potentials to more positive values. Cyclic voltammetry and differential pulse voltammetry clearly demonstrate one reversible oxidation and one reversible reduction wave with half wave potentials of −0.542 and −0.805 V for **4** in contrast to two reversible reduction waves

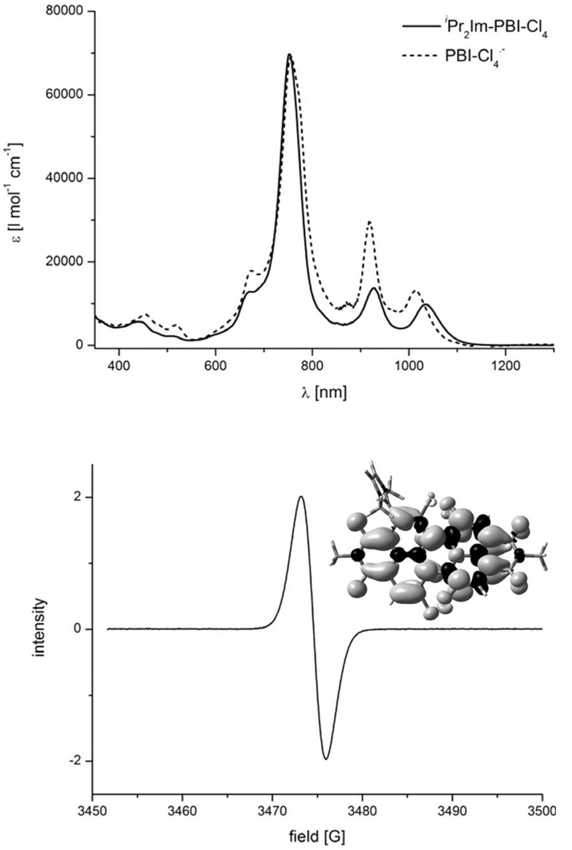


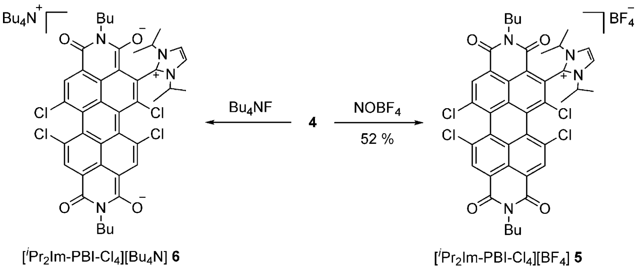
Figure 2. Top: UV/Vis absorption spectra of ^{i}Pr$_2$Im-PBI-Cl$_4$ **4** (in acetone, 1.00×10^{-5} mol l^{-1}; 298 K, solid line) and of electrochemically generated PBI-Cl$_4$ radical anion **1**$^{\cdot -}$ (in CH$_2$Cl$_2$, 5.50×10^{-4} mol l^{-1}; 298 K, dashed line). Bottom: EPR spectrum of ^{i}Pr$_2$Im-PBI-Cl$_4$ **4** in CH$_2$Cl$_2$ at 298 K (100 kHz magnetic field modulation of 0.1 Gauss and a microwave power of 0.63 mW). Spin density plot of a simplified model system (UB3LYP, 6-31+G*, isoval 0.0007 a.u.). Positive and negative spin is denoted by gray and black, respectively.

at −0.839 and −1.024 V for the PBI-Cl$_4$ starting material (Figure S10). For comparison, tetrachloro-substituted PBIs with two additional cyano groups at the *ortho*-positions are reduced at potentials of −0.50 and −0.81 V, whereas tetrachloro-tetracyano-substituted PBIs, which are the most electron-deficient perylene bisimide dyes, feature reduction potentials at −0.20 and −0.54 V.[7] Considering the energy level of ferrocene/ferrocenium with respect to the vacuum level, the SOMO (singly occupied molecular orbital) level of **4** can be estimated as (−4.8 + 0.54) eV = −4.26 eV.[8]

Since the proton NMR spectra of **4** revealed strongly broadened resonances (see above), EPR spectroscopy has been performed on a solution of **4** in dichloromethane. One intense resonance with a *g*-factor of $g_{\text{iso}} = 2.0036$ can be detected with no hyperfine coupling to the carbon or nitrogen nuclei of the aromatic core. Even though the absence of hyperfine splitting is less informative, this observation is consistent with the calculated spin density plot of a simplified model system (all alkyl groups are replaced by methyl) that indicates a complete delocalization of the unpaired electron over the whole PBI molecule with exception of the perpendicular-arranged imidazolium substituent (Figure 2, bottom).

Although all spectroscopic data discussed so far unambiguously prove the formation of the zwitterionic PBI-centered radical, the amount of **4** within the isolated product cannot be absolutely quantified by these methods. Regarding this uncertainty, the number of unpaired electrons per molecule has been investigated according to Evans method that is valid for isolated nonaggregated molecules in solution (see below).[9] NMR spectroscopy experiments were performed on a solution of **4** in CDCl$_3$ containing a flame-sealed capillary of pure CDCl$_3$. In the proton NMR spectrum two independent resonances for the solvent residual signals were detected at 7.26 and 7.28 ppm for the capillary and the paramagnetic solution, respectively. The paramagnetic shift of 6.96 Hz to lower field is caused by the PBI-centered radical and can be used to calculate the effective magnetic moment to 1.82 μ_B that correlates to 1.08 unpaired electrons (Figure S11). In combination with single-crystal X-ray analysis, high-resolution mass spectrometry, and elemental analysis, this result confirms the isolation of pure **4** and its delocalized radical character.

The reversible redox chemistry of **4** that has been quantified by cyclic voltammetry (see above) can also be extended to the preparative scale (Scheme 2). Upon titration of **4** with Bu$_4$NF[6g] a color change from green to blue can be observed accompanied by the increase of a new strong absorption band at 705 nm for the corresponding anion (Figure S12). However, due to the instability of the reduced species under ambient conditions [^{i}Pr$_2$Im-PBI-Cl$_4$][Bu$_4$N] **6** could not be isolated in pure form. In contrast, by adding two equivalents of nitrosyl tetrafluoroborate as the oxidant to a solution of **4** in chloroform, the orange oxidation product [^{i}Pr$_2$Im-PBI-Cl$_4$][BF$_4$] **5** can be isolated in good yield after column chromatography. This compound was easily characterized by multinuclear NMR as well as UV/Vis spectroscopy (Figures S13–S17).



Scheme 2. Chemical reduction and oxidation of ^{i}Pr$_2$Im-PBI-Cl$_4$ **4** to [^{i}Pr$_2$Im-PBI-Cl$_4$][Bu$_4$N] **6** and [^{i}Pr$_2$Im-PBI-Cl$_4$][BF$_4$] **5** with Bu$_4$NF and NOBF$_4$, respectively.

Single crystals of **5** were grown from a saturated chloroform solution to elaborate the structural differences between the radical **4** and the cationic **5** (Figure S18). All structural features of **5** regarding bond lengths and angles more closely resemble the neutral PBI-Cl$_4$ **1** than the zwitterionic **4** elucidating that the structural characteristics of **4** are rather caused by electronic than by steric effects (Table S1). Regarding the bond lengths within the cationic imidazolium substituent, no significant alterations can be ascertained (in contrast to the PBI core) indicating that the former electron has initially been located on the aromatic PBI core. This finding is consistent with an increased C=O stretch vibration of **5** at 1705 cm^{-1} in comparison to 1664 cm^{-1} for **4** (Figures S5–S7). The incorporation of counterions and solvent molecules between every second PBI leads to an alternating packing motive with π–π distances of 3.67 and 6.45 Å. In contrast to **4**, the cationic imidazolium substituent of **5** is arranged almost perpendicular to the PBI mean plane (87.3°) that is associated with a nearly symmetrical twist of the aromatic PBI core (34.2° and 34.6°).

In summary, we demonstrated a facile synthetic access to the first ambient stable zwitterionic perylene bisimide-centered radical that has been characterized by UV/Vis absorption, EPR, and NMR spectroscopy as well as single-crystal X-ray diffraction. This new compound can be reduced or oxidized reversibly to its corresponding anion or cation even on a preparative scale. Due to the remarkable chemical stability of this isolable PBI-centered radical, $^{i}Pr_2Im$-PBI-Cl_4 **4** constitutes a new prototype organic radical species[10] that might offer an entry into research on highly desirable ambient processable n-type dopants[11] for organic electronic devices.

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