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Facile Transformation of Perylene Tetracarboxylic Acid Dianhydride into Strong Donor−Acceptor Chromophores

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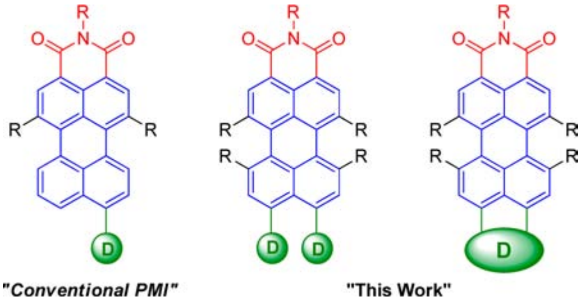
ABSTRACT



An efficient synthesis of 9,10-dibromo-1,6,7,12-tetrachloro-perylene-3,4-dicarboxylic acid monoimides from easily available 1,6,7,12-tetrachloro-perylene-3,4,9,10-tetracarboxylic acid dianhydride is reported. Therefrom, unprecedented perylene monoimides with pronounced donor−acceptor character were obtained via twofold aromatic amination. The halogen substituents in the 1,6,7,12-positions of perylene were removed under basic conditions. To the best of our knowledge, this is the first efficient synthetic route toward 9,10-doubly functionalized perylene-3,4-dicarboxylic acid monoimides.

The electronic absorption window is one of the most important criteria in dye stuff chemistry.[1] Great efforts have been continuously made to achieve near-infrared (NIR) or even infrared (IR) absorbers for potential applications in optical recording, NIR photography, laser welding, marking, bioimaging, and solar cells.[2] Several strategies have been utilized toward this goal. Among these are (i) extension of the π-conjugation,[3] (ii) polymerization,[4] (iii) formation of quinoid structures,[6] and (iv) incorporation of donor and acceptor substituents.[5] The design of push−pull systems has proven to be one of the most efficient ways to obtain large bathochromic shifts of the optical absorption.

Perylene-3,4-dicarboxylic acid monoimides (PMIs) and perylene-3,4,9,10-tetracarboxylic acid diimides (PDIs) are known as key chromophores in dye chemistry. Typically, they possess one or two imide entities as auxochromic groups which are responsible for their outstanding optical and electronic properties. Therefore, PMIs and PDIs play an important role as colorants and active components of organic electronic devices,[7] especially solar cells.[8,9] Under

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harsh imidization conditions in quinoline, using aliphatic or aromatic amines and $Zn(OAc)_2$, commercially available perylene tetracarboxylic acid dianhydride (PTCDA) can be directly transformed into PMI in reasonable yield.[10] Subsequently, the PMI can be either monobrominated (9-position) or tribrominated (1,6,9-position).[11] A method to selectively brominate the two *peri*-positions (9,10-position) is hitherto elusive. Via further nucleophilic substitution or metal-catalyzed coupling reactions, 9-monohalogenated PMIs can be functionalized with various substituents such as thiophene,[12] aromatic or aliphatic amines,[13] phenol,[14] carboxylic acid,[4a] and cyanide.[15] Our group, for example, has introduced different donors with varying electron-donating strength in the 9-position of PMI.[16] The resulting dyes exhibit absorption bands covering the whole visible and even parts of the NIR region.

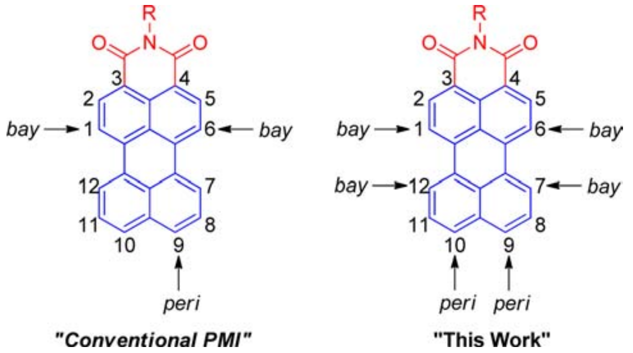
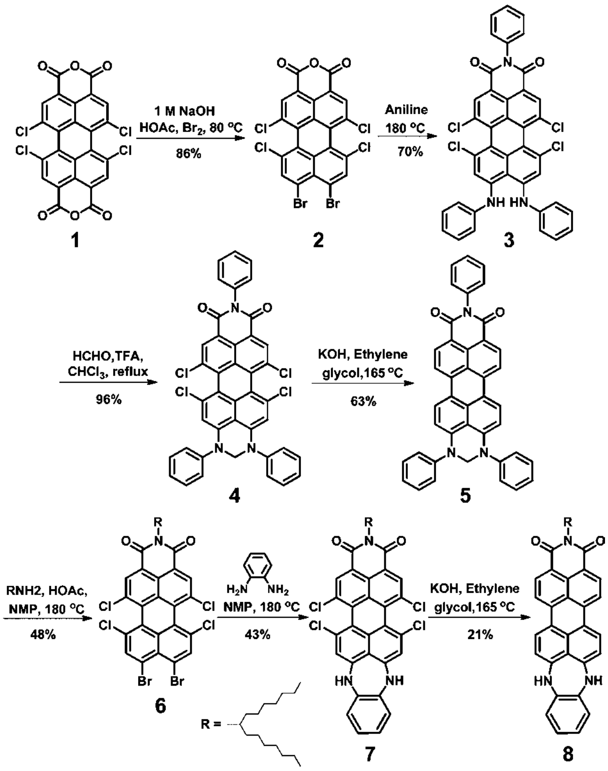


Figure 1. Design concept: comparison of conventional PMI and this work.

Besides the introduction of stronger donors in the 9-position, a donor functionalization of both *peri*-positions (9,10-position) would be a second promising way to enhance the push–pull character, compared to the current 9-donor-substituted PMIs,[16] due to increased electron density in the molecule. Very recently, a twofold donor functionalization of both *peri*-positions has been reported by Valiyaveettil.[17] However, the authors could not selectively introduce those functionalities but had to work with a mixture of isomers and tolerate *bay*-substitution. Donor functionalization of just the two *peri*-positions of PMI has not been reported yet and remains a great challenge due to the lack of a versatile building block. Bromination at the 9,10-positions of PMI is always accompanied by bromination of one or both *bay*-positions (1,6-position).[17] Additionally, the subsequent reactions of the brominated PMI normally take place first in the *bay*-positions. Here, for the first time, we describe a facile synthetic method toward 9,10-functionalized PMIs (Figure 1). To simultaneously introduce two donor groups in the *peri*-positions of the PMI skeleton, a selective Hunsdiecker reaction was carried out by a simple procedure, using inexpensive reagents i.e. sodium hydroxide, acetic acid, and bromine, as shown in Scheme 1.

Scheme 1. Synthesis of Double Donor PMI **5** and PMI **8**



Due to its flat and rigid core, the unsubstituted PTCDA is normally used as a pigment and is not soluble in most solvents. To ensure sufficient solubility of the intermediates, another commercially available 1,6,7,12-tetrachloro-PTCDA **1** was selected. The four chlorine substituents induce a twist in the perylene core and thus improve the solubility of **1** and its derivatives. The key building block, 9,10-dibromo-functionalized perylene monoanhydride **2**,

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was prepared in a high yield of 85% by a simple Hunsdiecker reaction,[18] by sequentially adding sodium hydroxide, acetic acid, and bromine to the PTCDA **1**. Compound **2** was slightly soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, THF, etc. The following one-pot reaction of **2**, in an excess amount of aniline, led to twofold aromatic amination and imidation, affording compound **3** in 70% yield. Subsequently, a methylene bridge between the amine donors was introduced (**4**) and the chlorine substituents were cleaved to give **5**. Compound **4** was prepared by cyclization with *para*-formaldehyde using catalytic amounts of trifluoroacetic acid (yield = 96%). In the following step, **5** was obtained by dechlorination of **4** using potassium hydroxide in ethylene glycol in 63% yield. Complete removal of the chlorine atoms was confirmed by both mass and NMR measurements (see Supporting Information).

It is known that aromatic diamines with adjacent amino groups can react with the anhydrides to form amidines.[19] For example, the reaction of **2** with 1,2-diaminobenzene in NMP produces benzimidazole due to the condensation of diamine and dicarboxylic acid anhydride, which additionally results in an unprecedented seven-membered ring formation by nucleophilic substitution of the two bromo-groups of **2** and 1,2-diaminobenzene. To avoid the condensation of dicarboxylic acid anhydride and 1,2-diaminobenzene, **2** was first transformed into its imide analogue **6** by imidation with pentadecan-8-amine in NMP at 110 °C. The following twofold aromatic amination of **6** with 1,2-diaminobenzene afforded PMI **7** in 43% yield. Further dechlorination of **7** was carried out using similar conditions as in the case of **4**, affording 21% of **8**.

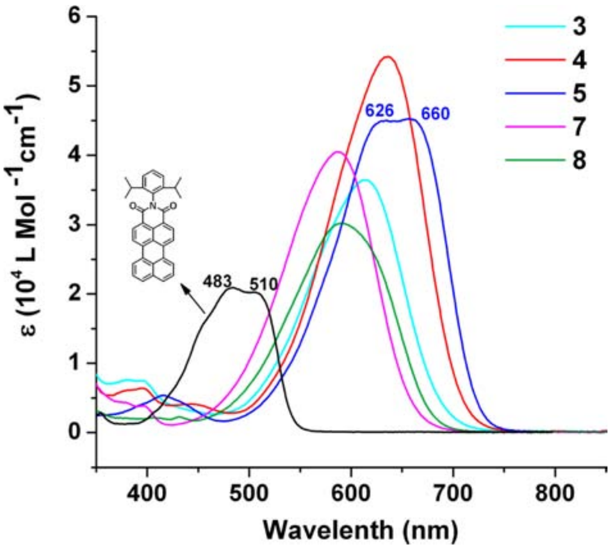

Figure 2. UV−vis spectra of PMIs **3**−**5**, **7**, and **8** in dichloromethane.

The UV/vis absorption spectra of compounds **3**−**5**, **7**, and **8** were recorded in CH_2Cl_2 solution. All double donor PMIs with 9,10-double functionalization exhibit broad absorption bands which is typical for push−pull type molecules. Compound **3** displays an absorption maximum around 612 nm. However, after bridging the nitrogen with a methylene group (compound **4**), not only is the absorption maximum shifted toward longer wavelengths (λ_{max} = 635 nm) but also the absorption band shows a considerably enhanced molar absorption coefficient (Table 1). Interestingly, the dechlorinated product **5** possesses a similar absorption spectrum as the unsubstituted PMIs (e.g., *N*-(2,6-diisopropylphenyl)-perylene-3,4-dicarboxylic acid monoimide, Figure 2 black curve) with two maxima at ca. 626 and 660 nm, which display a bathochromic shift of about 150 nm. In comparison to the unsubstituted PMI, **5** exhibits a similarly shaped absorption band, however, with a large bathochromic shift and strongly enhanced molar absorption coefficient, which indicates a synergistic pushing effect from the two symmetric donor groups in the 9,10-positions. Due to the push−pull effect, the fluorescence of compounds **5** and **8** is almost quenched. When excited at 660 nm, compound **5** shows a weak emission band with a maximum at 729 nm in CH_2Cl_2 solution and a quantum yield of 0.7%, while compound **8** exhibits an emission maximum at 677 nm when excited at 590 nm with a quantum yield of 0.2% (Figure S1, using Cresyl violet in ethanol as standard). These results indicate that an efficient photoinduced intramolecular electron transfer (PET) takes place in both compounds. The broad absorption bands in the vis−NIR region and additionally strong PET behavior show that **5** and **8** are outstanding candidates for application in photovoltaics, especially in dye-sensitized solar cells.

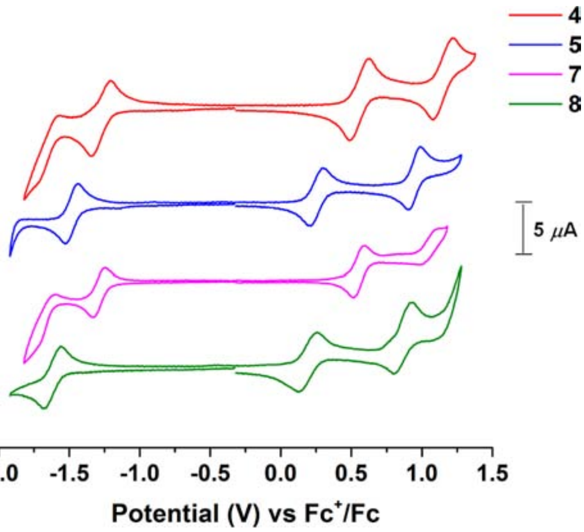

Figure 3. Cyclic voltammograms of **4**, **5**, **7**, and **8** in $CHCl_2$ with 0.1 M Bu_4NPF_6 as the electrolyte, AgCl/Ag as the reference electrode, Au disk as the working electrode, and Pt wire as the counter electrode with a scan rate of 100 mV s^{-1}.

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To elucidate the influence of the two phenylamino groups in the *peri*-positions on the energy levels of the molecular orbitals, the electrochemical properties of double donor PMI **4**, **5**, **7**, and **8** were investigated by cyclic voltammetry in CH_2Cl_2 (Figure 3). The onset potentials together with the calculated values for the HOMO–LUMO energy levels of **4**, **5**, **7**, and **8** are summarized in Table 1. For example, compound **4** shows two reversible oxidation curves at 0.48, 1.07 V and one reduction curve at −1.19 V (vs Fc^+/Fc), indicating stepwise formation of radical cations and dications upon oxidation and radical anions by reduction. In contrast, the dechlorinated compound **5** exhibits two reversible oxidation peaks with onsets at 0.18 and 0.88 V where the first oxidation onset is 0.3 V lower than that of **4**, suggesting that **5** is oxidized more easily than **4**. A similar decrease of oxidation and reduction potentials is observed for PMI **8** when compared to its chlorinated analogue **7**.

Table 1. Optical and Electronic Properties of PMIs

PMI	ε $[M^{-1}\,cm^{-1}]^a$	λ_{max} [nm]	E_{red1} $[V]^b$	E_{ox1} $[V]^b$	LUMO $[eV]^c$	HOMO $[eV]^d$
4	54200	635	−1.19	0.48	−3.61	−5.28
5	45300	660	−1.40	0.18	−3.40	−4.98
7	40500	588	−1.21	0.47	−3.59	−5.27
8	30200	591	−1.55	0.11	−3.25	−4.91

[a] Measured at λ_{max}. [b] Onset potentials, determined by cyclic voltammetric measurements in 0.1 M solution of Bu_4NPF_6 in CH_2Cl_2 vs Fc^+/Fc. [c] Estimated vs vacuum level from $E_{LUMO} = -4.80\ eV - E_{red1}$. [d] Estimated vs vacuum level from $E_{HOMO} = -4.80\ eV + E_{ox1}$.

In summary, we have presented the synthesis of two double donor substituted PMIs based on the versatile building block 9,10-dibromo-1,6,7,12-tetrachloro-perylene-3,4-dicarboxylic acid monoanhydride **2**, obtained by a selective Hunsdiecker reaction. This twofold peri-functionalization strategy opens up a new chapter in perylene chemistry regarding novel dyes, as well as perylene-based organic electronic materials. Remarkable push–pull systems with strong absorption toward the NIR can be achieved. Moreover, the different halogen functionalities in the *peri*- and *bay*-positions allow convenient fine-tuning of the molecular energy levels by further functionalization (e.g., phenoxylation, arylation or amination) instead of dechlorination. Imidation of **4** and **7** with designated anchoring groups such as glycine would allow use of these strong push–pull chromophores in dye-sensitized solar cells.[20] Introduction of such anchoring groups as well as a variety of other functional groups in the two *peri*-positions is currently underway in our laboratory.

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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.

The authors declare no competing financial interest.

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