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Syntheses and Properties of 1,6 and 1,7 Perylene Diimides and Tetracarboxylic Dianhydrides

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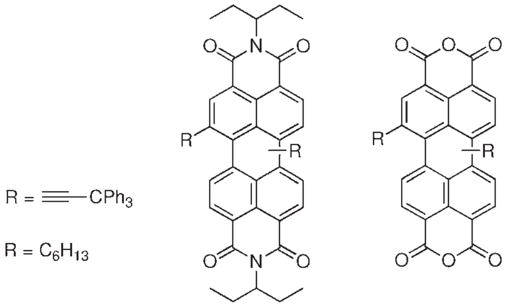
ABSTRACT



Chromatographically separable 1,6 and 1,7 regioisomers

Via Sonogashira cross-coupling with different alkynes, 1,6 and 1,7 perylene diimides (PDIs) and perylene tetracarboxylic dianhydrides (PTCDs) were synthesized from the corresponding regioisomeric mixture of 1,6/1,7-dibromo precursors. Both bulky triphenyl propyne (TPP) groups and nonbulky hexyl groups allow for facile chromatographic separation. The optical properties of these compounds are discussed. Neutral bay substituents hypsochromically shift both the absorption and emission through deformation from planarity of the perylene core.

Perylene tetracarboxylic diimides (PDIs) have received considerable attention in both academic and industrial research due to the favorable combination of large fluorescence quantum yields, high molar absorptivities, excellent thermal and photostability, chemical inertness and electron accepting properties.[1] Due to these desirable attributes, PDIs have been utilized in a variety of applications in the burgeoning field of organic electronics such as organic photovoltaics,[2] field effect transistors,[3] biosensors,[4] organic light emitting diodes,[5] optical switches,[6] and molecular wires.[7] PDIs have also been used in many other applications such as artificial photosynthetic systems[8] through controlled supramolecular architectures via their high propensity for π–π stacking.[9]

While the potential of the parent perylene tetracarboxylic dianhydride (PTCD) was known for decades, its utility was limited due to complete insolubility in organic solvents. PTCD becomes soluble via synthetic modification to *N*-alkyl

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or aryl PDIs and/or by modification of the "bay" region (1,6,7,12 positions).[10] Most research groups increase solubility by addition of bulky groups at the imide and fine-tune the electronic properties by functionalization of the bay region. Synthetically, however, this methodology has challenges that need to be addressed.

In 1997, BASF reported a procedure for the bromination of PTCD **1** at the 1,7 positions followed by imidization to afford PDIs of type **3**.[11] Upon formation of soluble PDIs, the bay bromines undergo a variety of substitution and cross-coupling reactions.[1a,12] Through this synthetic route PDIs were incorporated into dendrimers, organogels, and polymers, among others.[13] Unfortunately, all PDI publications prior to 2004 (and even some after) that reference BASF's bromination procedure for the synthesis of **1,7−3** should be regarded as using inseparable mixtures of 1,6 and 1,7 PDI derivatives.

In 2004, Würthner et al. drew attention toward the regioisomeric impurity of dibromo PDIs (**3**) and by deduction, dibromo PTCD.[14] Under the brominating conditions reported by BASF, the two regioisomers are actually synthesized in a ratio of ∼4:1. Unless the seminal 2004 Würthner et al. manuscript is referenced or there is pointed mention of removal of the 1,6-PDI impurity, it is difficult to determine whether or not the regioisomeric "problem" has been addressed.[15]

Although Würthner's method of separation is very useful, it is also time-consuming (6−8 weeks for pure **1,7−3**) and not amenable for separation of large quantities. Additionally, **1,6−3** cannot be isolated in pure form via the recrystallization process, and subsequently, little is known about its individual spectroscopic properties. There are only a few reports of isolation and characterization of both 1,6 and 1,7 bay substituted PDIs.[16] Herein, we present our approach for the synthesis, isolation and characterization of soluble 1,7 and 1,6 bay substituted derivatives of PDI and PTCD.[17]

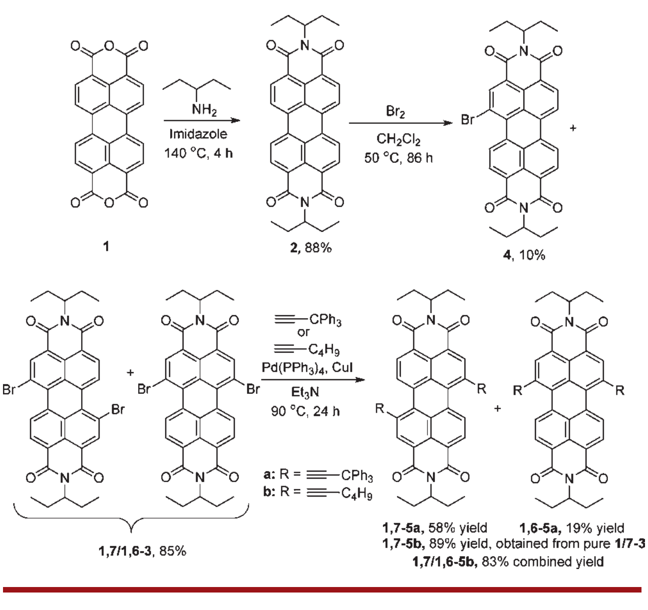
The spectral properties of PDIs change upon bay functionalization but, in solution, are only moderately affected by imide functionalization.[1c] The imide is hence an attractive synthetic handle for appending a myriad of supramolecular motifs for further self-assembly.[18] Following imidization and bay functionalization, PDIs can be converted back to the corresponding PTCDs, without losing solubility, for additional synthetic manipulation. In the quest to facilely obtain large quantities of pure 1,7 and 1,6 substituted PDIs, we investigated various neutral bay substituents to facilitate chromatographic separation of the regioisomers.

The syntheses of all reported compounds began with commercially available **PTCD-1** and are outlined in Schemes 1 and 2. Imidization of **1** with 3-aminopentane in imidazole at 140 °C afforded diimide **2** in 88% isolated yield. Bromination was achieved by heating diimide **2** with an excess of Br_2 (68 equiv) in CH_2Cl_2 for 48 h.[19] Under these conditions, the authors reported exclusive formation of **1,7/1,6−3**. In our hands, however, both the regioisomeric mixture (**1,7/1,6−3**) (70% yield) and monobromo **4** (28% yield) were formed (Scheme 1). The isolated yield of **1,7/1,6−3** was increased to 85% and the formation of monobromo **4** was reduced to 10% by prolonged reaction times. Pure **1,7−3** was isolated from the mixture following Würthner's procedure of repetitive recrystallization (7 weeks, 24% isolated yield).

To facilitate chromatographic separation,[20] we chose the base stable bulky triphenyl propyne (TPP)[21] group for bay substitution. Standard Sonogashira coupling conditions of 1,6 enriched **1,7/1,6−3** afforded the isomeric mixture of **1,7/1,6−5a** in 87% combined yield (Scheme 1).[22] **1,7−5a** and **1,6−5a** were easily separated by slow column chromatography over 7 days in good yield. The first band isolated was characterized as **1,6−5a** (19% yield) and the second band was characterized as **1,7−5a** (58% yield). Saponification of **1,7−5a** or **1,6−5a** afforded **1,7−6a** or **1,6−6a** in 73 or 75% respective yields (Scheme 2).[23]

It is .known that substitution at the bay region deforms the perylene core from planarity and can negatively

Scheme 1



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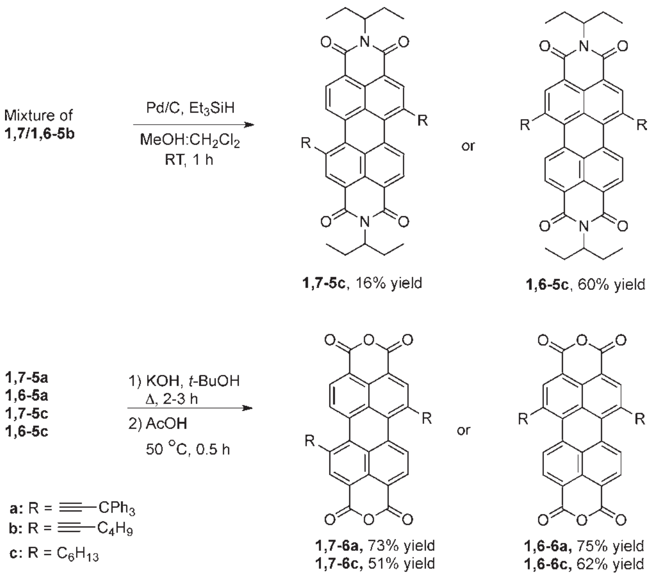
Scheme 2



affect solid-state packing and subsequent electron mobilities.[24] We were subsequently interested in appending less bulky groups. 1-Hexyne was cross-coupled to the bay region of the regioisomeric mixture of **3** (Scheme 1).[2b,12b,25] As expected, **1,7–5b** and **1,6–5b** could not be differentiated by TLC or separated by column chromatography.

Using **1,7–3** obtained from crystallization and subsequent Sonogashira cross-coupling, **1,7–5b** was isolated in 83% yield. We attempted to obtain the corresponding PTCD **1,7–6b** by saponification, however, the harsh basic conditions decomposed **1,7–5b** and no isolable products were obtained. To circumvent this problem, the regioisomeric mixture of **1,7/1,6–5b** was subjected to palladium-catalyzed hydrogenation.[26]

To our surprise, the two regioisomers **1,7–5c** and **1,6–5c** were easily separable by conventional column chromatography in just a few hours. Contrary to the original hypothesis, bay substitution with bulky groups is not a requirement for facile separation of PDIs. Alkyl substituted PDIs **1,7–5c** and **1,6–5c** were converted to the respective PTCDs via saponification to afford **1,7–6c** and **1,6–6c** in 51 and 62% yields (Scheme 2). All compounds (**1,7/1,6–5,6**) exhibit excellent solubility in a variety of solvents such as CH_2Cl_2, $CHCl_3$, toluene, THF, DMSO, acetone etc.

The steady state absorption spectra of all 1,7/1,6 PDI and PTCD derivatives were obtained in CH_2Cl_2 (Figure 1). The values of the absorption maxima and the corresponding molar extinction coefficients are given in Table 1. Compounds with alkynes appended at the bay region (**1,7/1,6–5a,b-6a**) have an absorption maxima between 545–555 nm, which is red-shifted from the parent PDI **2** (524 nm). Upon reduction, the absorption maxima hypsochromically shift to 520 and 521 nm respectively. The moderate blue shifts of **1,7/1,6–5c** and **6c** are due to deformation by the alkyl groups as it is known that deformation from planarity of the perylene core results is hypsochromic shifts.[27] We attribute these shifts primarily to steric and not electronic effects as the neutral hexyl substituted compounds, **1,7/1,6–5c** and **6c**, are blue-shifted even when compared to electron withdrawing bay substituted PDIs (–CN, Cl, Br)[1d,12b] and have similar λ_{max} as 1,7 dinitro substituted PDIs,[28] most of which have been shown via crystallography to be deformed from planarity. However, it is difficult to ascertain to what extent electronic and/or steric effects contribute to shifts in the absorption spectra of PDIs and PTCDs.

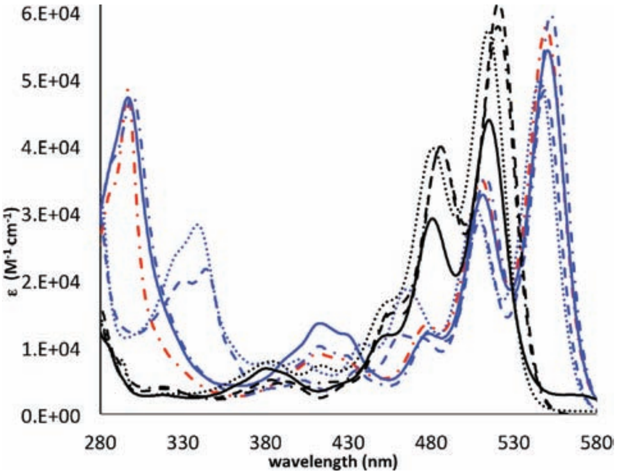


Figure 1. Steady state absorption spectra of PTCDs and PDIs (1.0×10^{-5} M, 25 °C, CH_2Cl_2). Blue: R = TPP. Red: R = hexyne. Black: R = hexyl. **1,7-PDIs** = dot-dash line; **1,6-PDIs** = dashed line; **1,7-PTCDs** = solid line; **1,6-PTCDs** = dotted line.

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Table 1. Physical Data for All PDIs and PTCDs Synthesized

compound[a]	λ_{max} [nm]	ε [M^{-1} cm^{-1}][b]	λ_{em} [nm][c]	T_d [°C][d]	T_c [°C][e]	T_m [°C][e]
1,7–5a	552	59490	571	380	N.D.	N.D.
1,6–5a	549	48200	566	375	N.D.	N.D.
1,7–5b	549	57620	570	N.D.[f]	N.D.	N.D.
1,7–5c	521	61210	542	357	N.D.	N.D.
1,6–5c	520	57750	541	357	N.D.	N.D.
1,7–6a	550	54140	571	381	NA[g]	NA
1,6–6a	546	49420	565	390	NA	NA
1,7–6c	515	43770	535	340	248	207
1,6–6c	514	57110	536	340	242	213

[a] Optical properties measured in CH_2Cl_2. [b] Determined at λ_{max}. [c] Excited at λ_{max}. [d] Determined by TGA. [e] Determined by DSC. [f] N.D. = not determined. [g] NA = no observed phase transitions in temperature range investigated.

The predominant difference between alkynyl substituted 1,7 and 1,6 regioisomers is evident at ≈295 nm and ≈330 nm. We attribute the absorbances at ≈295 nm to the 1,7 substitution pattern with alkyne conjugation while the ≈330 nm absorption band is attributed to conjugated 1,6 substitution. Neither of the absorbances are present in the reduced compounds (Figure 1). **1,6/1,7–5c** and **6c** do not show any significant differences between the two regioisomers. Additionally, converting PDIs **1,7/1,6–5c** to PTCDs **1,7/1,6–6c** does not induce any significant changes in the absorption spectra. PTCD pairs **1,7/1,6–6a** or **1,7/1,6–6c** have nearly identical λ_{max} in solution, however, these regioisomeric pairs exhibit solid state-chromy indicative of dissimilar $\pi-\pi$ stacking in the solid state.[29]

The emission spectra of all PDIs and PTCDs were recorded and the wavelength of the emission maxima are given in Table 1. The emission spectra are typical for PDIs[30] and do not exhibit any major differences between the 1,7 and 1,6 regioisomers. As with the absorption spectra there is little difference between the bay substituted PDIs and PTCDs. Stokes shifts are also similar among the compounds and only minimal solvatochromism is observed (see Supporting Information).

The thermal stability of PDI and PTCD derivatives were measured with thermogravimetric analysis (TGA) (Table 1). Alkyne substituted PDIs and PTCDs **1,7/1,6–5a** and **6a** have decomposition onset temperatures ≥375 °C. Alkyl substituted **1,7/1,6–5c** and **6c** have much lower decomposition onset temperatures (340–360 °C). We compared the morphological behavior of **1,7/1,6–6a** and **6c**, with differential scanning calorimetry (DSC). The corresponding values are given in Table 1. PTCDs **1,7/1,6–6a** do not show any thermal transitions in the temperature range investigated (25–300 °C). DSC of **1,7/1,6–6c** show the presence of both melting and crystallization temperatures. In comparison to the TPP subsituted compounds, PTCDs **1,7/1,6–6c** show phase transitions presumably due to the presence of the hexyl chains, which impart mobility and thus afford melting and crystalline phase transitions.

In summary, we have reported on the syntheses, facile separation techniques and properties of 1,7 and 1,6 regioisomers of bay appended PDIs. In addition, we reported on the syntheses and properties of both 1,7 and 1,6 bay substituted PTCDs. Alkyl bay substituted PDIs and PTCDs had previously been unreported and have attractive spectral and solubility properties. Additional solid state and electrochemical data will be published in due course in a corresponding full manuscript.

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

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