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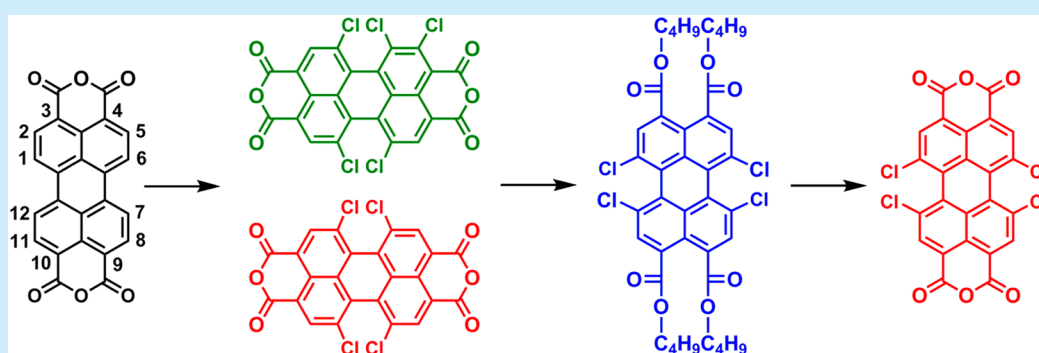
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Facile Synthesis of Pure 1,6,7,12-Tetrachloroperylene-3,4,9,10-tetracarboxy Bisanhydride and Bisimide

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S Supporting Information



ABSTRACT: A robust and scalable procedure to obtain pure 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxy bisanhydride, a highly valuable synthon, has been developed via synthesis of a novel intermediate compound 1,6,7,12-peryene-3,4,9,10-tetracarboxy tetrabutylester.

Perylene bisimide (PBI) dyes have been the subject of great interest in both industrial and academic domains because of their outstanding optoelectronic properties.¹ Bay-area substitution of the perylene core (1, 6, 7, and 12 positions), with two or four substituents, has further enhanced the importance of PBIs, as it provides additional advantageous properties. First, this substitution increases the solubility by twisting the planar perylene core, which reduces their tendency to undergo π - π stacking. Second, it modifies the optoelectronic properties, which is not possible by substitution at other positions.^{1a,b,2}

There are two well-established procedures to obtain bay-functionalized PBIs.³ The first method involves the controlled bromination of perylene bis-anhydride (PBA, **1**) to the corresponding 1,7-dibromoperylene derivatives.⁴ Subsequently, the bisanhydride is converted in a bisimide, and bromo atoms can be replaced by various substituents to afford PBIs with desired properties and good solubility. The major setback for this procedure has been the presence of a substantial amount of 1,6-regioisomeric impurity, which is often difficult to remove.⁵ The second procedure, the tetrachlorination of PBA by chlorosulfonic acid, has been considered a straightforward method to obtain pure 1,6,7,12-tetrachloro-PBA.⁶ The chloro atoms, after imidization, can be substituted easily with phenoxy groups to give core-twisted PBIs with excellent solubility. Over the course of time, the tetrachloro-PBIs have been widely used in the preparation of many interesting systems.^{1b,7}

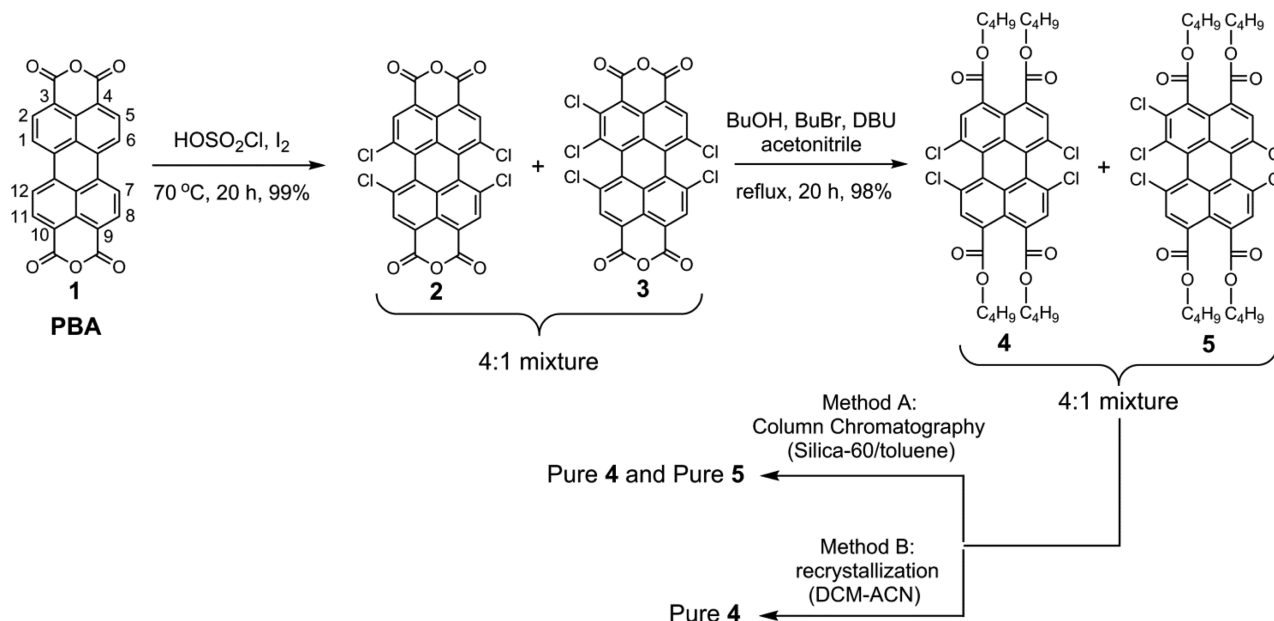
In this study, we have found that the conventional laboratory procedure for tetrachlorination of PBA using chlorosulfonic acid yields substantial amounts of side products. To the best of our knowledge, this issue of contamination has been reported only in one occasion.⁸ In our view, this problem did not receive attention from the research community because (i) the poor solubility of 1,6,7,12-tetrachloro-PBA in common organic solvents has prevented thorough characterization and (ii) the contaminants in 1,6,7,12-tetrachloro-derivatives are difficult to detect by ¹H NMR spectroscopy. Pure 1,6,7,12-tetrachloroperylene derivatives may have been obtained from 1,6,7,12-tetrachloro-PBA after further reaction and purification steps, i.e. imidization and/or substitution of the chloro-atoms.⁹ However, it would be most desirable to start the synthesis of bay-functionalized PBIs with pure 1,6,7,12-tetrachloro-PBA. Therefore, in this work, we have developed a new and facile procedure to synthesize pure 1,6,7,12-tetrachloro-PBA.

Chlorination of commercially available PBA **1** was carried out using chlorosulfonic acid at 70 °C following the conventional laboratory procedure (Scheme 1).⁶ The crude product was investigated by the 400 MHz ¹H NMR spectroscopy in concentrated D₂SO₄. The NMR spectrum exhibits the expected singlet for the four perylene-core protons of 1,6,7,12-

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Scheme 1. Chlorination of PBA 1 Followed by Esterification To Produce Chlorinated Perylene Tetrabutylesters



tetrachloro-PBA 2 at 8.75 ppm, along with a small singlet at 8.78 ppm and another small singlet that overlaps with the main singlet (Figure 1). This indicates the presence of at least one

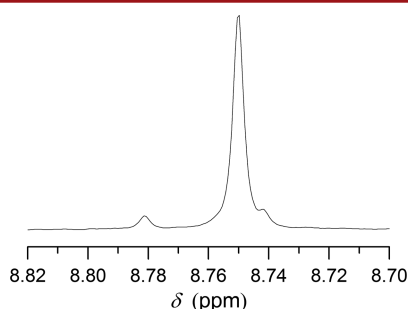


Figure 1. ^1H NMR spectrum (400 MHz, D_2SO_4) of crude chloro-PBA (2 + 3).

additional compound in the crude product. Further analysis by high-resolution mass spectrometry revealed that the side product is 1,2,6,7,12-pentachloro-PBA 3.

To remove the impurities, the crude mixture containing compounds 2 and 3 was submitted to a Soxhlet extraction with dichloromethane, but no noticeable change in the composition has been observed. Keeping in mind the poor solubility of bisanhydrides 2 and 3 in organic solvents, no further purification attempts have been carried out. Changing the reaction conditions, notably reducing the reaction time or reaction temperature, did not prevent the formation of tri- and/or pentachloro-PBA (Table S1).

To obtain pure tetrachloro-derivatives, we decided to convert the crude mixture of 2 and 3 into the corresponding perylenetetrabutyl ester derivatives¹⁰ (PTEs), as these are highly soluble and crystalline compounds which can be transformed back to bisanhydride after purification.^{5d,11} The esterification reaction gave a mixture of tetra- and pentachloroperylene tetrabutylester 4 and 5 in 98% yield (Scheme 1). In the 850 MHz ^1H NMR spectrum (Figure 2a), the main singlet from the tetrachloro-PTE 4, is accompanied by two

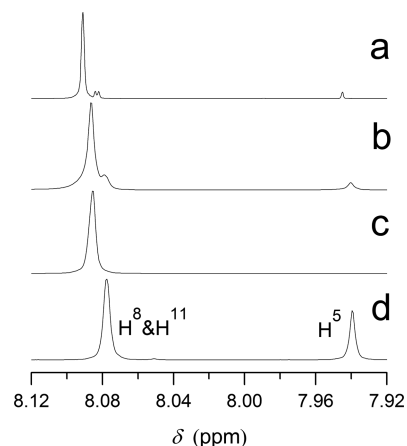


Figure 2. ^1H NMR spectra (aromatic region) in CDCl_3 : (a) Mixture of 4 and 5 obtained at 850 MHz; (b) Mixture of 4 and 5 obtained at 400 MHz; (c) Pure 4 obtained at 400 MHz; (d) Pure 5 obtained at 400 MHz.¹²

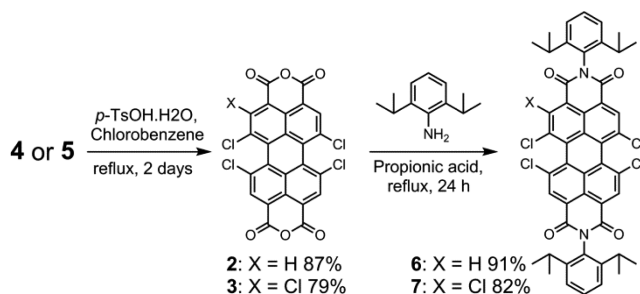
small singlets at ca. 8.07 and another small singlet at 7.94 ppm. These additional singlets originate from H8 and H11, and H5, respectively, of the pentachloro derivative 5. Based on the integration, the pentachloro-derivative 5 is present in 20% quantity. It should be noted that, in the 400 MHz spectrum (Figure 2b), only the H5 singlet of compound 5 is well separated from the large singlet of the four equivalent protons of compound 4. Therefore, the contamination of 4 by 5 appears to be very small because the intensity ratio of both resonances is 18:1 whereas the product ratio is 4:1.

TLC analysis of the crude mixture of 4 and 5 in toluene revealed two well separated spots. Subsequently, isolation of pure tetrachloroperylene tetrabutylester 4 and pentachloroperylene tetrabutylester 5 was achieved by column chromatography (Scheme 1). ^1H NMR spectra of pure tetrachloro 4 and pentachloro 5 perylene tetrabutyl ester are shown in Figure 2c and d. The desired tetrachloro-derivative 4 was also obtained in pure form by repetitive recrystallization from an acetonitrile/dichloromethane mixture. Pure compound 4 is usually afforded

after three crystallizations in a yield of ca. 40%. Higher yields can be obtained by further workup of the filtrate obtained after each crystallization. It is important to note that the crystallization-based purification process is highly suitable for the synthesis of pure compound **4** on a multigram scale.

Finally, the pure tetrachloroperylene tetrabutylester **4** was converted back to the corresponding bisanhydride **2** in high yield (87%) by an acid catalyzed removal of the four ester moieties in refluxing chlorobenzene (Scheme 2). The purity of

Scheme 2. Synthesis of Pure Tetra- and Pentachloroperylene Bisanhydrides (**2** and **3**) and Bisimides (**6** and **7**)



the obtained bisanhydride **2** was confirmed by ¹H NMR spectroscopy (Figure S1). Pure perylene bisanhydride **2** is a valuable and highly versatile synthon that provides direct access to many pure 1,6,7,12-tetra bay-functionalized perylene derivatives. To prove this point, bisanhydride **2** was converted to bisimide **6** by an imidization reaction with 2,6 diisopropylaniline in a 91% yield as shown in Scheme 2.¹³ The pentachloro-PBA **3** and the pentachloro-PBI **7** were synthesized using the same synthetic procedure (Scheme 2).

Imidization of the crude chlorinated PBA, containing compounds **2** and **3**, was also carried out to obtain a mixture of tetra- and pentachloro-PBIs **6** and **7** (Scheme S1). In the ¹H NMR spectrum of the mixture of PBIs **6** and **7**, a large amount of pentachloro compound **7** can be detected only by the small additional resonance of HS in the aromatic region (Figure S4). TLC analysis in different eluents did not show separation of PBIs **6** and **7**. Therefore, these tetra- and pentachloro-PBIs could not be obtained in pure form by column chromatography, when prepared from a mixture of **2** and **3**.⁹ Here, it should be noted that the tetrachloro-functionalized PBIs (e.g., **6**) cannot be reconverted to tetrachloro-PBA **2**, by the cleavage of the imide functionalities using concentrated KOH.¹⁴ This is due to the harsh reaction conditions which will affect the chloro substituents.^{6a,15} Therefore, obtaining the tetrachloro-PBI in the pure form will not be a versatile approach for obtaining the pure tetrachloro- perylene derivatives.

The optoelectronic properties of compounds **4**–**7** have been investigated by absorption and fluorescence spectroscopy in chloroform (Table 1). The absorption spectra of all four compounds are dominated by π – π^* transitions in the visible

Table 1. Physical Properties of Compounds **4**–**7** in Chloroform

compd	λ_{abs} (nm)	ϵ (M ^{−1} cm ^{−1})	λ_{em} (nm)	Φ_f	τ_f (ns)	mp (°C)
4	457	23 000	503	0.25	1.6	164
5	456	22 000	500	0.15	1.0	126
6	522	30 000	550	0.98	4.9	>350
7	521	28 000	556	0.95	5.3	>350

region (Figure 3). However, in the case of tetra-ester derivatives **4** and **5**, the characteristic fine structure is significantly

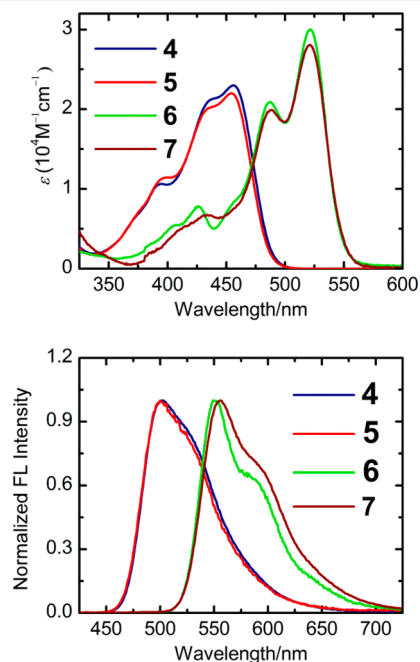


Figure 3. UV/vis absorption and normalized emission spectra of compounds **4**–**7** in chloroform.

reduced.¹⁶ In addition, a substantial reduction has been observed in the fluorescence quantum yield and lifetime of compounds **4** and **5** with respect to PBIs **6** and **7**. Interestingly, significant differences have also been observed in the optical properties of the two tetraester compounds **4** and **5**. The fluorescence quantum yield and lifetime are found to be lower for the pentachloro derivative **5**, when compared to corresponding tetrachloro compound **4**. For the bisimides **6** and **7** the differences in optical properties are limited to a small red shift in emission and a slight increase in fluorescence lifetime for the pentachloro-PBI **7**. These preliminary results clearly reflect the significant effect of the chlorine substitution pattern on the physical properties of these compounds. Thus, only from pure compounds, (photo)physical properties can be determined accurately.

In conclusion, our study reveals that the conventional laboratory procedure to synthesize 1,6,7,12-tetrachloroperylene bisanhydride **2** inevitably produces other chloro-substituted products, which are difficult to detect and hard to remove. Therefore, we have developed a new synthetic strategy to obtain pure 1,6,7,12-tetrachloroperylene bisanhydride **2** in multigram quantities via the synthesis of a novel intermediate compound 1,6,7,12-tetrachloroperylene tetrabutylester **4**. Spectroscopic studies have revealed a significant difference in optical properties between tetrachloro- and pentachloroperylene derivatives, notably in fluorescence quantum yields and lifetimes. Further studies focusing on the scope of pure 1,6,7,12-tetrachloroperylene tetrabutylester **4** as a synthon to synthesize novel 1,6,7,12-tetrachloro-functionalized perylene derivatives, with interesting optoelectronic properties, are currently underway and will be reported in due course.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures and full characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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