Perylene monoanhydride diester: a versatile intermediate for the synthesis of unsymmetrically substituted perylene tetracarboxylic derivatives

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ABSTRACT

A soluble perylene monoanhydride diester has been designed and synthesized. It was successfully utilized as an efficient intermediate for the synthesis of the first unsymmetric perylene tetracarboxylic tetraester and a series of unsymmetric perylene diester monoimides in good to excellent yields. Its application in synthesis of unsymmetric perylene diimides was also demonstrated. Availability of such a versatile intermediate would enable the convenient integration of perylene tetracarboxylic tetraesters and perylene biester monoimides into intricate functional molecular systems.

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Perylene tetracarboxylic acid-based dyes are under intense investigations due to their promising applications. In particular, N,N′-disubstituted perylene tetracarboxylic diimides (PDIs) have been widely used as lightfast colorants,[1] highly efficient fluorophores,[2] the electron acceptor in solar cells,[3] the active component in field effect transistors,[4] liquid crystalline materials,[5] and versatile building block in self-assembly.[6] Structurally related tetraesters of perylene tetracarboxylic acids (PTEs) were also reported as liquid crystals,[7] fluorescent dyes,[2b] the electron acceptor in light harvesting systems,[8] and light emitting diodes.[9] Similar to PDIs, PTEs have appreciable electron-accepting power, and are capable of forming perylene π-stacks in both solutions[10] and the solid state.[11] Recently, perylene tetracarboxylic diester monoimides (PEIs), where an imide and two ester groups connect to the same perylene core, have also attracted considerable attention as more soluble alternatives to PDIs.[12] Nevertheless, comparing with PDIs, the scope of applications of PTEs and PEIs is rather limited. Reports on PTEs are limited to symmetrically substituted tetraesters, whereas PEIs have been explored only in the form of simple alkyl derivatives recently. In contrast, besides simple symmetrically substituted derivatives, PDIs have also been extensively incorporated into complex molecular and supramolecular architectures.[13–18] This is probably because there are a number of methods by which unsymmetrically substituted PDIs can be readily accessed.[19] Contrarily, systematic synthetic strategies for PEIs have not been well developed, and there are no reports on unsymmetrically substituted PTEs. From a materials scientist's point of view, it is important to be able to integrate PTEs and PEIs into more structurally intricate systems, especially those with light harvesting capabilities, considering the surging interest in organic photo-

voltaic materials. In order for a donor/acceptor organic photovoltaic system to achieve the optimal energy conversion efficiency, the electron acceptor should have an appropriate electron affinity that matches the electron donor.[20] Among three types of perylene derivatives, PTEs are the weakest electron acceptors, while PDIs are the most powerful ones. Thus, being able to use PTEs or PEIs to replace the PDIs in photovoltaic systems provides a unique way to *tune* the electron-accepting power of the acceptor for the best possible conversion efficiency, in addition to the substantially improved solubility in common organic solvents. This calls for the capacity to access unsymmetrically substituted PTEs and PEIs. Herein, we report the design and synthesis of perylene tetracarboxylic monoanhydride diester **1**. It can serve as a versatile intermediate for the synthesis of unsymmetric PTEs and PEIs, as well as PDIs.
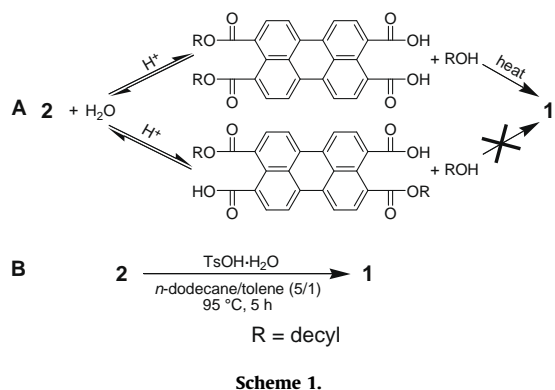
Compound **1** is intrinsically unsymmetric. The reactivity difference between the anhydride and the ester groups is great enough for a nucleophile to selectively attack the anhydride group. Two flexible decyl groups provide the necessary solubility in organic solvents, which facilitates purification and characterization.

R = decyl
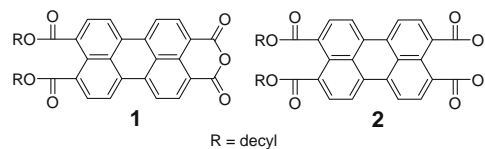
It was envisioned that **1** could be prepared from a symmetrically tetrasubstituted PTE **2** via either basic or acidic hydrolysis. The acid-catalyzed route is chosen because of its potential high yield as depicted in Scheme 1A. First, an acid-catalyzed hydrolysis reaction is a reversible reaction. Therefore, even if the initial ester bond cleavages did not occur at the 'right' positions, they could be

Scheme 1.

Table 1
Condensation of **1** with amines

Entry	R'NH₂	Reaction condition	Product (% yield)
1	(2,6-dimethylheptan-2-amine, branched) NH₂	120 °C, 3 h	(**3a**, 99%)
2	Ammonium decanoate	120 °C, 1 h	(**3b**, 88%)
3	H₂N—⬡—OH	130 °C, 3 h, DMAP	(**3c**, 85%)
4	H₂N (serinol) with two OH	130 °C, 1.5 h	(**3d**, 79%)

R = decyl.

"corrected" through the esterification-hydrolysis equilibrium. Second, at a relative high temperature (typically >90 °C), a unimolecular cyclization reaction occurs rapidly giving a six-membered cyclic anhydride once two carboxyl groups formed from a **2** molecule are at the 'correct' positions. This removes **1** out of the esterification-hydrolysis equilibrium and contributes to a high yield. To obtain the highest possible yield, further hydrolysis of the ester groups in **1** must also be avoided. One approach is to use a solvent that dissolves **2** well but hardly dissolves **1** at the reaction temperature. In this way, **1** may precipitate from the solution upon its formation, which slows down the further cleavage of the ester groups in **1**. It has been found that a mixture of *n*-dodecane and toluene (5:1 v/v) is well suitable for this purpose. Finally, reaction time must also be controlled to maximize the yield of **1**. The optimized reaction condition is given in Scheme 1B. A high concentration (~0.62 M) of **2** and 1 equiv of p-toluenesulfonic acid monohydrate (TsOH·H₂O, serving as the acid catalyst and the water source) reacted at 95 °C for 5 h giving **1** in a satisfactory (74%) isolated yield. Compound **2** was prepared in an excellent yield (97%) according to a slightly modified literature procedure.[21]

The identity of **1** has been confirmed by ¹H NMR, FT-IR, HRMS, and UV (see Supplementary data). **1** dissolves in various common organic solvents such as chloroform, dichloromethane, toluene, acetone, THF, and pyridine. Although its room temperature solubility in most solvents (except chloroform) is low (~10^{-4} M), the solubility increases substantially in warm or hot solvents. In molten imidazole, a widely used solvent for imidization reactions of perylene anhydrides, **1** dissolves considerably at 100 °C affording a bright red solution at about 10^{-2} M concentration. This implies that the condensation of **1** with primary amines will be smoother than that of perylene tetracarboxylic dianhydride which is insoluble in any organic solvents.

To demonstrate the applicability of **1** for the synthesis of unsymmetric PEIs, it was condensed with four amines as shown in Table 1. Four new PEIs were obtained in good to excellent yields, which confirms the suitability of **1** as a precursor of unsymmetric PEIs. It is worth mentioning that a large excess of amine is not necessary to achieve a high yield. This is practically important especially when the primary amine must be prepared by a multi-step synthesis. When a less reactive amine (entry 3) is used, the reaction can be significantly accelerated by adding 4-dimethyl-aminopyridine (DMAP) (Supplementary data). The use of DMAP as the general acylation catalyst is well documented. However, to the best of our knowledge, it has not been applied to the reactions involving perylene anhydrides. Probably, this is because the low solubility of perylene tetracarboxylic dianhydride was the major limiting factor for most of such reactions. For **1**, such a solubility limitation is lifted so that the nucleophilic attack to carbonyl may become the rate-limiting step which can be catalyzed by DMAP.

PEIs **3b**, **3c**, and **3d** can serve as reactive intermediates that can be readily integrated into a larger structure. This is illustrated by
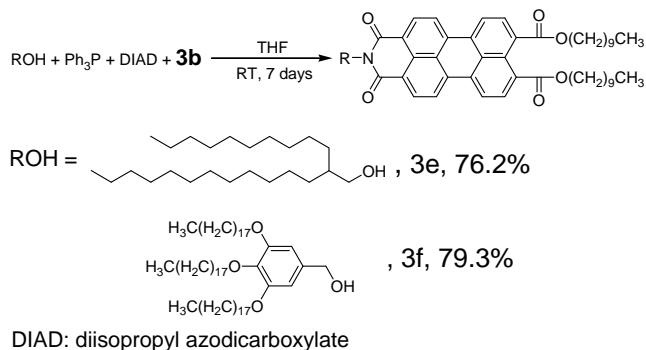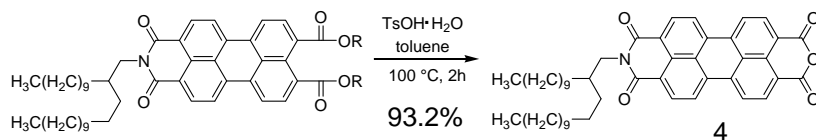
the successful installation of substituents at imide nitrogen atom of **3b**. Due to the mild acidity of the imide proton, nucleophilic substitution reactions of **3b** can be carried out after deprotonation. However, in many cases, the Mitsunobu reaction with an alcohol is preferred as alcohols are often more readily available than their halide/sulfonate or amine counterparts. Two such reactions are presented in Scheme 2 with good yields.
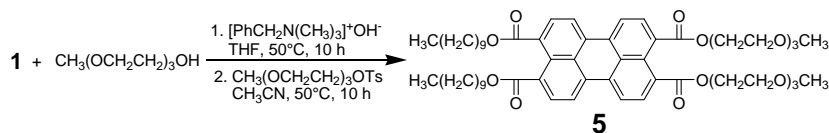
In addition to serving as the less electron deficient, more soluble alternatives to PDIs, PEIs can also be converted to perylene tetracarboxylic monoimide monoanhydrides which are the precursors of unsymmetric PDIs. The ester groups in a PEI are less stable than the six-membered cyclic imide group, and thus can be selectively cleaved under either acidic or basic conditions. The feasibility of

ROH = (branched long-chain alcohol) OH , 3e, 76.2%

(trialkoxybenzyl alcohol, H₃C(H₂C)₁₇O groups) OH , 3f, 79.3%

DIAD: diisopropyl azodicarboxylate

Scheme 2.

Scheme 3.

Scheme 4.

Table 2
The first reduction potentials of perylene tetracarboxylic derivatives versus Fc/Fc⁺

Compound	E_1 (V)	Compound	E_1 (V)
1	−1.162	**3a**	−1.311
2	−1.589	**3b**	−1.256
4	−0.988	**3c**	−1.255
5	−1.568	**3d**	−1.214
6	−1.044	**3e**	−1.333
		3f	−1.284

this transformation is supported by the high-yield reaction shown in Scheme 3.

Another unique application of **1** is that it can act as the precursor of unsymmetric PTEs. The availability of **1** made it possible to synthesize the first unsymmetrically substituted PTE **5**, as outlined in Scheme 4. The good overall yield (80%) signifies the effectiveness of **1** as the precursor of unsymmetric PTEs.

Finally, electron-accepting powers of different perylene tetracarboxylic acid derivatives were examined electrochemically. Their first reduction potential values are listed in Table 2. For the purpose of comparison, the first reduction potential of PDI **6**[5d] with the structure shown below was also measured. As expected, the perylene monoimide monoanhydride **4** is more electron deficient than **6**, as the anhydride group is more electron withdrawing than the imide group. For the same reason, the electron affinity of **1** is greater than that of PEIs. The two PTEs, **2** and **5**, are the least electron-deficient materials due to four least electron-withdrawing ester groups. As expected, six PEIs exhibit intermediate electron affinity between the PTEs and PDI **6**. It is quite interesting to observe that the difference in first reduction potential values among PEIs is as great as 0.119 V. Evidently, the availability of unsymmetric PEIs and PTEs as PDI alternatives will allow one to tune the acceptor electron affinity to a considerable degree, which may help minimize the energy loss during the electron transfer from the donor to the acceptor in an organic photovoltaic system.[20]

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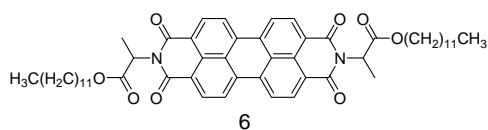
In conclusion, we have designed and successfully synthesized a soluble perylene tetracarboxylic monoanhydride diester. This compound can serve as the versatile intermediate for the synthesis of novel unsymmetrically substituted PTEs and PEIs which could be further converted to unsymmetric PDIs. The ability to access unsymmetric PEIs, PTEs, and PDIs would enable molecular engineering of complex organic functional systems having the electron acceptor with tuneable electron affinity, which may lead to the optimum optoelectronic performance.

Acknowledgments

Supplementary data

Supplementary data (detailed experimental procedures, spectroscopic data and NMR spectra of final products) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.11.084.

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