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Direct synthesis of highly pure perylene tetracarboxylic monoimide

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ABSTRACT

A series of perylene tetracarboxylic monoimides substituted with cycloalkanes were synthesized through a one-step reaction between cycloalkyl amines and the parent perylene dianhydride. The reaction demonstrates high selectivity for the production of monoimides with no formation of diimides. The high reaction selectivity is primarily due to the insolubility of the monoimides in the reaction medium, which in turn causes rapid precipitation of the products, shifting the reaction equilibrium to the right.

Perylene tetracarboxylic diimides (PTCDIs) represent a robust class of *n*-type organic semiconductor with high thermal and photo-stability, and have long been used in various optoelectronic materials and devices.[1–4] As evidenced in recent research, appropriate side-chain modification of PTCDIs facilitates one-dimensional (1D) cofacial stacking of the molecules, leading to formation of well-defined nanowires or nanobelts.[4–7] Compared to the traditional bulk-phase materials, these 1D nanostructures often demonstrate unique properties and unprecedented performance, such as 1D confined charge transport,[8–10] linear emission polarization,[11,12] and 1D enhanced exciton migration, and the resulted amplification of emission quenching.[13,14] Combination of these optoelectronic properties enables applications in vapor sensing of gaseous reagents through modulation of the emission intensity or electrical conductivity of the nanofibers.[4,15]

The synthesis of PTCDIs takes advantages of the fact that the two nitrogen positions at the imides of PTCDI are nodes in the π-orbital wavefunction,[16] providing enormous options for modifying the structures of the two side-chains (but without significant altering of the electronic property of the PTCDI skeleton). To construct supramolecular structures of PTCDI containing multifunctional moieties (e.g., electron donor for charge separation, hydrophilic side-chain for enhanced layer-by-layer stacking), it is often demanded to make the monoimide as precursor so as to synthesize the asymmetric PTCDIs with two different side-chain substitutions (Chart 1). However, most of the monoimides have thus far been synthesized through partial hydrolysis of the symmetric PTCDI,[17,18] followed by extensive column purification (which could be extremely time-consuming and costly if the solubility of imides is limited). This prevents large scale production of the asymmetric PTCDIs for the necessary materials fabrication. To overcome this bottleneck, it is critical to develop a synthetic protocol that allows for direct preparation of monoimides from the parent dianhydride compound (Chart 1).

Herein we report on a one-step synthesis of highly pure cycloalkyl substituted monoimides without further purification (Scheme 1). Cycloalkanes represent a special class of side-chains that possess a crossed orientation with the perylene plane at about 90°, thus enforcing rotated stacking between the molecular planes so as to minimize the steric hindrance caused by the cycloalkanes rings.[12] The rotated stacking enables strong fluorescence emission for the nanofibers thus fabricated from the molecules, though most of other PTCDIs demonstrate very weak emission due to the H-type π–π interaction.[3]

In one typical reaction, perylene-3,4,9,10-tetracarboxylic dianhydride (0.2 g, 0.51 mmol), cyclohexylamine (0.5 mL, 4 mmol),

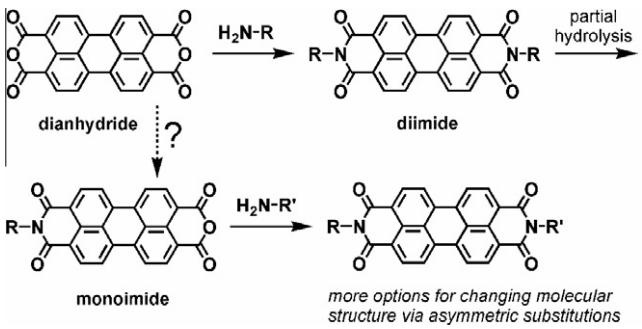

Chart 1. Synthetic pathways for PTCDIs.

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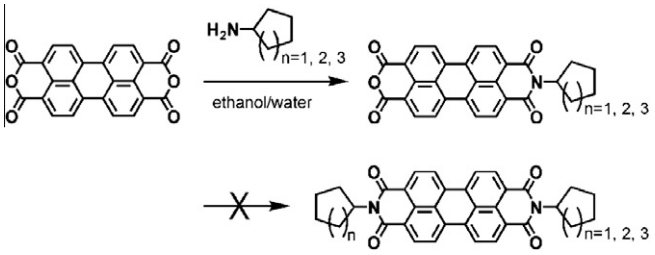
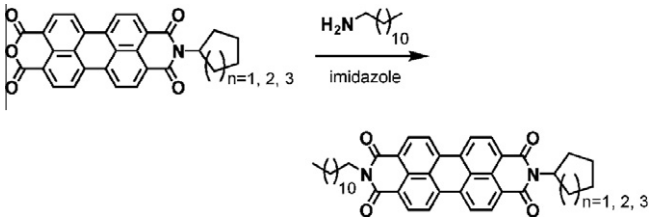


Scheme 1. One-step condensation leading to selective production of monoimides.



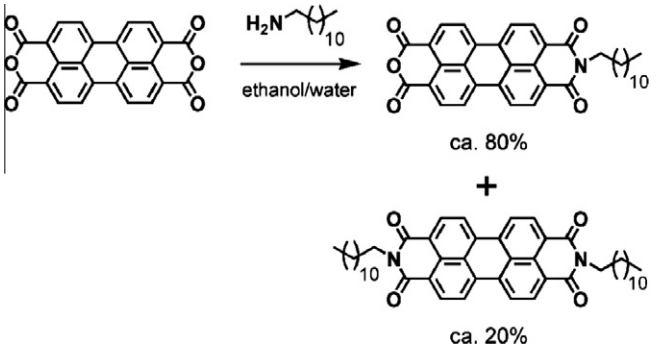
Scheme 2. Substituting the monoimides with long alkyl side-chains to improve the solubility for NMR characterization.

and ethanol/water (20 mL, volume ratio of 4:1) were mixed and heated at 70 °C for 6 h. The reaction mixture was cooled to room temperature and acidified by adding 30 mL concentrated HCl (12 M) and 20 mL water. After stirring overnight, the resultant solid was collected by vacuum filtration through a 0.45 μm membrane filter (Osmonics), followed by washing with methanol and water until the pH of washings turned to be neutral. The collected solid was dried in vacuum at 60 °C. The solid thus obtained was proven pure with no formation of the diimide, which has significant solubility in chloroform and can be spotted (if any) by alumina TLC (eluent: chloroform/methanol of 9:1).

Since the solubility of cycloalkyl monoimide in common organic solvents is very low, it is impossible to perform NMR characterization directly on the monoimide products obtained. To improve the solubility, the as-prepared monoimides were reacted with excessive dodecylamine to convert into the asymmetric di-substituted PTCDIs (Scheme 2), which turned to be sufficiently soluble in chloroform, allowing for ^{1}H NMR characterization.[22] As evidenced for all the three PTCDIs substituted with cyclopentyl, cyclohexyl, and cycloheptyl, the NMR spectra showed clean assignment to a single compound, which in turn indicated the high purity of the monoimide as prepared in Scheme 1. The straight, highly selective production of monoimides thus observed is largely due to its insolubility in the mixed solvent of ethanol/water, which causes rapid precipitation of the product out of the reaction medium. Such precipitation-driven synthesis was previously employed in the preparation of macrocyclic conjugated molecules through cyclo-oligomerization.[19,20]

To further prove the concept of precipitation-driven synthesis, we changed the reaction medium from ethanol/water mixture to other alcohol based solvents, where the cycloalkyl PTCDIs remain insoluble.[12] These solvents include pure ethanol, methanol, and their mixtures with water containing varying levels of water up to 60%. As expected, the only product for the reaction following the same protocol described above (Scheme 1) was the corresponding monoimide. Increasing the water content above 60% makes it difficult to dissolve the alkyl amines, thus significantly slowing the reaction process.

The same reaction protocol was also tested for synthesizing other monoimides substituted with different side-chains such as dodecane (Scheme 3). The reaction turned out not as selective as



Scheme 3. One-step condensation with linear alkyl amines shows decreased selectivity for the production of monoimides.

that performed with the cycloalkyl side-chains. In the best case (14:6 ethanol/water), the production yield of the dodecyl monoimide was only about 80%, with 20% parallel production of the diimide. This less selective reaction is likely due to the increased solubility of dodecyl monoimide in alcohols. Indeed, as previously observed in propanol/water mixture, the same reaction also produced diimide as impurity.[21]

In conclusion, a series of perylene tetracarboxylic monoimides substituted with cycloalkyls were synthesized through a one-step reaction between cycloalkyl amines and the parent perylene dianhydride, both of which are cheap and commercially available. The high selectivity thus obtained for the reaction is primarily due to the insolubility of the monoimides in the reaction medium, which in turn causes rapid precipitation of the products. This precipitation-driven synthesis may be extended to preparation of other perylene monoimides, for which selection of appropriate reaction medium is the most critical for achieving the high purity of product. In general, an ideal reaction medium must possess minimal (if not none) solubility for the monoimides, while still maintaining sufficient solubility for the reactant amines.

Acknowledgments

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22. The asymmetric PTCDIs substituted with dodecyl and three different cycloalkyl groups were synthesized following the standard condensation method previously developed (see Refs. 4,17). In a typical reaction, 193 mg (0.41 mmol) of the cyclohexyl substituted monoimide, 113 mg (0.61 mmol) of dodecylamine, and 2 g of imidazole were heated at 120 °C under argon for 4 h. The reaction mixture was cooled to room temperature and dispersed into 10 mL ethanol, followed by addition of 25 mL of 2 M HCl. After stirring overnight, the resulting solid was collected by vacuum filtration through a 0.45 μm membrane filter (Osmonics). The red solid was then washed thoroughly with methanol and water until the pH of washings turned to be neutral. The collected solid was dried in vacuum at 60 °C. TLC: R_f (silica gel/CH_3Cl:methanol 95:5) = 0.60. The purity and structure of the three asymmetric PTCDIs thus prepared (as shown in Scheme 2) were confirmed by ^{1}H NMR as presented below:
N-cyclopentyl-N′-dodecyl-perylene-3,4,9,10-tetracarboxylic diimide. ^{1}HNMR (500 MHz, $CDCl_3$): δ = 0.87 (t, 3H, CH_3), 1.24–2.28 (m, 28H, 14CH_2), 4.11 (t, 2H, CH_2), 5.53 (t, 1H, CH), 8.15 (m, 8H, perylene). Yield: 92%.
N-cyclohexyl-N′-dodecyl-perylene-3,4,9,10-tetracarboxylic diimide. ^{1}HNMR (500 MHz, $CDCl_3$): δ = 0.87 (t, 3H, CH_3), 1.24–2.28 (m, 30H, 15CH_2), 4.16 (t, 2H, CH_2), 5.04 (t, 1H, CH), 8.44 (m, 8H, perylene). MALDI–TOFMS gave *m*/*z* 640.3 (calculated 640.33). Yield: 90%.
N-cycloheptyl-N′-dodecyl-perylene-3,4,9,10-tetracarboxylic diimide. ^{1}HNMR (500 MHz, $CDCl_3$): δ = 0.87 (t, 3H, CH_3), 1.24–2.28 (m, 32H, 16CH_2), 4.17 (t, 2H, CH_2), 5.20 (t, 1H, CH), 8.50 (m, 8H, perylene). Yield: 91%.