Reactive Bay-Functionalized Perylene Iimide: Synthesis, Structure and Characterization

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Abstract. N,N'-di(2-ethylhexyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide have been synthesized from the novel Perylene bisimides (Perylene-3,4,9,10-perylene tetracarboxylic acid diimides) and ethylhexylamine and characterized with HNMR, FT-IR and UV-Vis; it can be used for further substitution at the bay position without any further capping group. Dibrominated perylene diimide bay-substituted derivates tends to aggregate strongly in dilute solutions. Because of its ability to be further substituted at the bay region with other desired functional groups, photo-induced behavior and electron mobility indicates that perylene diimide is indeed a promising material for use in processing of organic based semiconductors. Dibromo moieties on the 1, 7 bay area leads to twisting of the perylene core, weakens the \(\pi-\pi\) stacking thus improving its solubility.

Introduction

In recent past, donor-acceptor conjugated complexes or oligomers have attracted intense scientific investigation due to their unique optical, strong absorption\cite{1} and electrical properties with potential applications in many fields such as molecular electronics\cite{2, 3}, optoelectronics\cite{4, 5}, sensors\cite{3, 6} and thin-film transistors\cite{7}.

Perylene bisimides represent a class of highly thermo-stable\cite{8, 9} n-type semiconductors\cite{4} with relatively high electron affinity\cite{10} and excellent transport property. Much attention has been focused on the modification and functionalization of PDI structures at bay positions through high-yield synthetic routes to improve their chemical\cite{11} and physical\cite{11} properties. These PDIs and their derivatives have been used not only as building blocks for electronics\cite{5, 12} and optoelectronics devices such as organic light emitting diodes\cite{13}(OLEDs), light-harvesting arrays\cite{14}, photovoltaic cells\cite{3, 8, 15} but also for studying the photoinduced energy and electron-transfer process\cite{9}.

Generally PDI has a large \(\pi\)-system\cite{13, 16}, hence making the material susceptible to stacking. The stacking hinders the development of ordered solid structures of PDI, limiting its solubility in organic solvents\cite{2, 8}, which is an important aspect of processing electronic devices\cite{17}. PDI have a large core aromatic chromophore and in turn possess strong sol-vophilic and \(\pi-\pi\) stacking forces\cite{18}. Stacking can be reduced by constraining the \(\pi-\pi\) intermolecular interactions\cite{19} by functionalizing it at the bay area, which leads to twisting of the \(\pi\)-conjugation, weakening the \(\pi-\pi\) stacking interactions\cite{20} significantly. PDI derivatives with bulky substitutes on the N, N’ – imides provide steric hindrance to PDI core, which can greatly reduce the stacking\cite{21} thus significantly improving its solubility\cite{11}.

Most of n-type organic molecules have poor solubility \cite{19, 22} in organic solvents\cite{7, 17}, however due to its improved electronic properties in solution state and simple methods for fabricating it in electronic systems, makes it a major field of interest. Soluble PDIs have attracted attention for the processing of OTFT\cite{23, 24}. Perylene 3,4,9,10-tetracarboxylic acid diimide, is one of the promising material because its molecular structure can be used to change the substituents on
the N atoms in imide or on the bay positions[3, 5, 25]. Substituting functional groups on PDI bay position and imide positions improve several properties, such as electrochemical and electronic properties and can also improve solubility which then allows for the construction of organic based electronics. Furthermore, having the lowest unoccupied molecular orbital (LUMO)[21, 23, 25] level makes PDI derivatives have strong electron affinities[2, 21]. when the N atoms of the imide position is substituted, an inductive effect is achieved whereas bay position substitution leads to twisting of planar geometry and induces intermolecular charge transport[26]. Organic phototransistors have outstanding characteristics of low temperature fabrication and flexibility[25].

Herein, we prepared N,N’-di(2-ethylhexyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide from 1,7-dibromoperylene tetracarboxylic acid anhydride and 2-ethylhexylamine in pyrrolidine.

Figure 1. Synthesis procedure for N,N’-di(2-ethylhexyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide.

Perylene diimides functional dyes have unique n-type properties which makes them to be the best organic n-type semiconductors. These classes of dyes are planar with strong π-π interaction forces which make them prone to aggregation[12] and poor solubility[22, 27]. Bulky substitution at the N-imides can sterically hinder the π-π interaction and make the dye more soluble. The solution UV-Vis absorption and photoluminescence properties of the N,N’-di(2-ethylhexyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide are similar to those of the unsubstituted PDI. However, the inherent stacking tendency in PDI is greatly suppressed, as aggregation studies have depicted, this allows the PDI chromophore to crystallize into highly ordered single structures[5]. The crystals, unlike the parent solid PDI, have enhanced solid fluorescence[26, 28], excitation in the visible region[28] and are highly soluble in organic solvents. These properties are very important in developing PDI based optoelectronic devices. While there has been a success in attaching ethylhexylamine on the imide position of bay area brominated PDI, more recrystallization work needs to be done as to separate 1,6 and 1,7 bay substitution as to fully exploit this approach. In this line of thought we have synthesized N,N’-di(2-ethylhexyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide molecule with reactive bromine, mainly at 1,7 bay positions.

Experimental

Materials

2-ethylhexylamine (TCI (shanghai) Development Co.ltd, ≥98%), pyrrolidine (shanghai lingfeng chemical reagent Co.ltd, ≥99.5%), distilled water, PTCDA (ZTO Co.ltd, ≥98%), sulfuric acid (J&K
Chemical ltd, 95-98%), Iodine (sinopharm chemical Reagent Co.ltd, ≥99%) All organic solvents used (J&K Chemical ltd) and tetrahydrofuran (THF) were used as received without further purification.

### Synthesis of N, N'-di(2-ethylhexyl)-1,7-Dibromoperylene-3,4,9,10-Tetracarboxylic Acid Bisimide

PTCDA\textsubscript{Br} was synthesized by bay area functionalization of PTCDA in a single step condensation reaction with bromine in concentrated sulphuric acid following previous reference. N,N’ -di(2-ethylhexyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide was synthesized as outlined in Figure. 1, using the following method to obtain a mixture of 1.7 (major) and 1.6 (minor): 0.95g of 2-ethylhexylamine and 2.58g (2.55 mmol) PTCDA\textsubscript{Br}, a crude mixture of 1,7-dibromoperylene 3,4,9,10-tetracarboxylic acid bisimide and 1,6-dibromoperylene 3,4,9,10-tetracarboxylic acid bisimide, are dissolved in 30 ml Pyrrolidine and 100 ml distilled water in a round bottom flask and fitted with a condenser. Under an Argon atmosphere, the mixture was then heated under reflux in an oil bath at 90°C with vigorous stirring for 4 hrs. It was then cooled to room temperature. The collected product was then subjected to suction filtration to obtain red solid. The product was dried in an oven. The target product, N,N’ -di(2-ethylhexyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide was obtained by purification using column chromatography with trichloromethane and petroleum ether to give a yield of about 76%.

**N,N’ -di(2-ethylhexyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic Acid Bisimide:**

- FT-IR (KBr) 3428, 2917, 2519, 2360, 2340, 1773, 1726, (s, C=O), 1660 (s, C=O), 1590, 1371, 1139, 1040 and 492 cm\(^{-1}\)

- \(^1\)H NMR (400 MHz, CDCl\(_3\)); \(\delta \) 9.43 (d, J ) 8.2 Hz, 2H, perylene-H), 8.87 (s, 2H, perylene-H), 8.65 (d, J ) 8.1 Hz, 2H, perylene-H), 4.09-4.19 (m, 4H, -CH2-N), 1.92-1.96 (m, 2H, -CH-), 1.32-1.42 (m, 16H, -CH2-), 0.95 (t, 6H, -CH3), 0.90 (t, 6H, -CH3).

### Equipment and Sample Testing

The NMR spectra were measured on a Bruker 400 MHz NMR spectrometer with chloroform (CDCl\(_3\), J&K chemical Ltd ≥ 99.8) as a solvent. The \(^1\)H NMR spectra were referenced to the residual proton impurities in the CDCl\(_3\) at 6 7.27 ppm. The UV-Vis spectra were recorded on a Lambda 35 (Perkin Elmer) spectrophotometer. The emission and excitation spectra of the samples were investigated on a FP-6600 steady-state fluorescence spectrophotometer. All the measurements were carried out in room temperature with ambient air.

### Results and Discussion

#### Molecular Design and Synthesis

Perylene diimides functional dyes have unique n-type properties which makes them to be the best organic n-type semiconductors. These classes of dyes are planar with strong \(\pi-\pi\) interaction forces which make them prone to aggregation and poor solubility. Bulky substitution at the N-imides can sterically hinder the \(\pi-\pi\) interaction and make the dye more soluble. The orientation of 2-ethylhexylamine molecule with a \(\pi\)-conjugated is expected to exhibit better packing of molecules to form solid structures with good solid state fluorescence. PTCDA, the parent material for making PDI has two anhydride reactive ends. Substitution of the two anhydride end results in perylene diimide dihydride. Diimidization of PDI improves the properties of PDI such as solubility. However, dibromo functionalization of PDI at the bay area is an important process because it allows for incorporation of various desired further substituents on PDI core for electronic modification. Dibromo moieties leads to twisting of the perylene plane, thus significantly weakens the \(\pi-\pi\) stacking interactions. Presences of N,N’-di(2-ethylhexyl)-1, 6-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide was depicted on HNMR analysis, as earlier stated, separation of N,N’-
di(2-ethylhexyl)-1, 7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide and N,N'-di(2-ethylhexyl)-1, 6-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide is a bit tedious.

Molecular characterization of the product confirmed the success of the synthetic procedure. The presence of imide C=O stretching at 1773, 1726 and 1660, 1590 cm$^{-1}$, respectively, plus C–O stretching peak at 1034 cm$^{-1}$ on the FT-IR spectrum, were a clear indication of PDI diimide compound. Further confirmation of successful synthesis of N,N'-di(2-ethylhexyl)-1, 7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide was verified by $^1$H NMR, whereby the respective protons was identified as 8.87 (s, 2H, perylene-H), 8.65 (d, $J$ 8.1 Hz, 2H, perylene-H), 4.09-4.19 (m, 4H, -CH$_2$-N), 1.92-1.96 (m, 2H, -CH-), 1.32-1.42 (m, 16H, -CH$_2$-).

**Photophysical properties of N, N'-di(2-ethylhexyl)-1, 7-dibromoperylene-3,4,9,10-tetracarboxylic Acid Bisimide in Solution**

Modification of PDI photophysical properties strongly depends on the nodes at the imide position. Incorporating ethylhexylamine on the N-imide has been reported to drastically change the characteristic solution UV-Vis absorption and photoluminescence properties of PDI. Diimidization of PDI with ethylhexylamine as well as bay functionalizing it with bromine to form N,N'-di(2-ethylhexyl)-1, 7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide is expected to change the luminescent and solid state absorption properties positively. The solubility of N,N'-di(2-ethylhexyl)-1, 7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide in different organic solvents was tested using UV-Vis absorption spectra and the results have been shown in Figure.2. The sample showed good solubility in all the tested solvents, which had varying polarity. The parent PDI usually shows limited solubility in organic solvents, which is limited only to polar solvents. In our case, N,N'-di(2-ethylhexyl)-1, 7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide had good solubility in both polar solvents, like chloroform, and non-polar solvents, such as hexane. The good solubility indicates that the usually strong π-system interactions have been weakened resulting in easy solvation in the different solvents. Solution self-assembly of conjugated molecules can be used to investigate the strength of π-π interaction forces. Strong forces will tend to cause the molecules to start aggregating in very low concentrated solutions, while weak forces will only cause the molecules to start aggregating at a much higher concentration in solution.

![Figure 2. UV-Vis absorption spectra on different solvents.](image)

The self-assembly of N,N'-di(2-ethylhexyl)-1, 7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide was tested by varying its concentration in toluene and chloroform respectively from $3.71 \times 10^{-5}$ M to $4.6 \times 10^{-7}$ M and measuring the corresponding solution fluorescence spectra. The results are described in Figure.3. From the solution absorption spectra it can be seen that all the spectra within the tested concentration retained the same characteristic shape, only the peak intensity increased with an increase in concentration.
Figure 3. UV-Vis absorption spectra; a) Different concentration in toluene, b) Different concentration in chloroform.

Excitation emission of the free molecules at 450 nm[16] is evidence due to the conversion into crystal phase, while excitation of the crystal phase at 570 nm results in no emission as evidenced by the zero intensity scanning line.

Figure 4. Fluorescence spectra in hexane; fluorescence intensity increases with concentration.

Self-assembling N,N’-di(2-ethylhexyl)-1, 7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide molecules into one-dimensional structures represents a balance between molecular stacking and solubility. Sufficient solubility in some solvents is crucial for processing the self-assembly[29] of PDIs from individual molecules, this is achieved by incorporating appropriate side chains, in this case Ethylhexylamine, this expands the size of the PDI core system by hindering the π–π stacking hence weakening the π-conjugation. The twisting between the N,N’-di(2-ethylhexyl)-1, 7- bromoperylene-3,4,9,10-tetracarboxylic acid bisimide in the supramolecules weakens the π–π interaction between molecules and thus contorts the packing arrangement from the ideal face-to-face configuration. Strong π–π stacking configuration normally leads to strong bonding, resulting in low-energy excitonic transition, making non-emitting crystal phase.

Conclusion

We have successfully synthesized N,N’-di(2-ethylhexyl)-1, 7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide with bromine reactive group at the bay area, bromine readily reacts with OH groups and thus these molecules are an ideal system for processing dimensional optoelectronic properties of organic semiconductor materials. Bromine leads to twisting (with an angle twist of 24.10°)[20] of the perylene core, weakens the π–π conjugation. We can also conclude that imidization of PTCDABr at both ends improves solubility as well as hindering π–π stacking. A balance between molecular stacking and sufficient solubility[30], self-assembly, is a key to Processable n-type semiconductors; to which we have achieved.
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Reference


