



# Impact of alkyl chain and bay-phenoxy unit on the sensing performance of perylene diimide derivatives



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## ARTICLE INFO

### Article history:

Received 23 June 2016

Received in revised form 9 November 2016

Accepted 3 December 2016

Available online 5 December 2016

### Keywords:

Perylene diimide derivatives

Nanostructure

Sensory properties

Core-substituted groups

Structure-property relationship

## ABSTRACT

In this contribution, three perylene diimide derivatives (PDIs) substituted on the 1,6,7,12-positions with phenoxy groups were prepared, on which the substituted groups are tetraphenoxy (pH), *para*-*tert*-butylphenoxy (TpH) and *para*-tetramethylbutylphenoxy (OpH). Studies on their sensing properties in hydrazine vapor (5 ppm) suggested these materials have good sensing performance. In these three PDIs, OpH shows the best sensing performance owing to its better crystalline structure, smallest torsion angle and activation energy with face-to-face stacking mode. A well-ordered crystalline structure with smaller interplanar spacing and modest activation energy leads TpH exhibiting middle-grade of sensing performance in these PDIs. While the largest activation energy, a greater torsion angle with poor crystalline structure induce the least-efficiency sensing performance of pH sensors. This study indicates the aromatic groups, the length and branched point of alkyl chain on bay region have significant impact on sensing performance of PDIs devices by modulating crystalline structure,  $\pi$ - $\pi$  overlap and energy level.

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## 1. Introduction

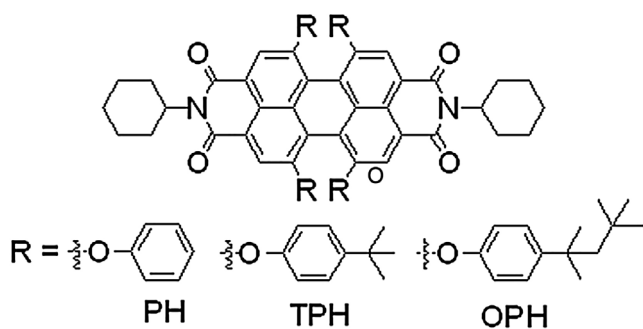
Perylene diimide derivatives (PDIs) have been extensively used in optoelectronic devices owing to their excellent chemical and thermal stability [1,2], especially as organic field-effect transistors [3,4], solar cells [5–8] and sensors [9–18]. In order to improve the performance of PDIs devices, molecular modification is usually considered as one of the most important means. In this respect, chemical modifications of PDIs core on the imide N-, bay- and *ortho*-position(s) have been reported [19]. Among these three chemical modification possibilities, functionalization on the bay-position(s) has been proved to be the most efficient and feasible way to achieve high-performance PDI devices. To date, covalently linked bay substituent groups, such as aromatic or heteroaromatic rings, can tune the orbital energy levels and the energy gap of the resulting PDIs system [6]. Moreover, the steric hindrance of the substituent also affects the  $\pi$ - $\pi$  overlap and intermolecular  $\pi$ - $\pi$  stacking of the perylene core, which can significantly influence the electron mobility of the solid-state material [13–15]. Therefore, functionalization on bay-positions with chemical groups provides the possibility of modulating the physical, optical, elec-

tronic and aggregation properties of the obtained materials, and thus the in-depth understanding of structure–property relationship can be efficiently achieved. However, in practice, finding such structure–property relationship has been so far difficult. The substituted groups have to be carefully selected to obtain an appropriate balance between the desired electronic properties and geometric shape to attain all the required characteristics.

Optimal molecular design of organic semiconductors via side chain engineering has led to remarkable advances in high-performance devices [20,21]. This is because the length [22], branching point position [23], and bulkiness [24] of side chains can critically affect the physicochemical properties of organic semiconductors (i.e., solubility, optical absorption capacity, and solid state packing) and consequently influence molecular packing and the  $\pi$ -planar distance that are closely related to device performance. In practice, some interesting results indicated that even a subtle change in the length, substitution position and bulkiness of alkyl chains might have a significant influence on device performance. For instance, Pei and co-workers reported the enhancement of charge mobility for isoindigo-based conjugated semiconductor after varying the branching alkyl chains by separating the branching point away from the conjugated backbone [25]. Oh et al. observed the odd–even effect of the alkyl side chain spacers on diketopyrrolopyrrole-based molecular packing and the charge transport [26]. Wang and co-workers discovered the substitution

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**Scheme 1.** Chemical structure of pH, TpH and OpH.

with the longer alkyl chains on the N-positions of tetrachlorinated di(perylenediimide) could produce higher electron mobilities in air [4]. Because the roles of alkyl chains in organic semiconductors are quite complex and highly dependent on the conjugated backbones, it is expected that the integrated consideration and engineering of both perylene core and flexible chains will greatly affect the performance of PDIs devices.

In our previous work, we have systematically studied the impact of 1,7-substituted aromatic groups on PDIs sensing performance [27–29]. The results revealed that aromatic groups on the bay-positions can remarkably affect the energy level, packing mode and interplanar spacing of solid materials so as to have significant impact on PDIs gas response. In recent work, we prepared four PDIs bearing alkylsilane chains on 1,7-substituted positions with different lengths and branched points in order to probe the effect of alkyl chains on sensing performance [14]. Our study indicated that the length and branched point of alkylsilane on the bay region play a vital role in determining the performance of PDIs devices by variation of torsion angle of perylene core,  $\pi$ - $\pi$  interplanar spacing and aggregation mode. These interesting results motivate us to conduct further investigation about the effect of 1,6,7,12-tetraphenoxy-substituted groups on PDIs sensing performance through combining the aromatic group and alkyl chain.

In the present study, three perylenediimide derivatives: *N,N'*-dicyclohexyl-1,6,7,12-tetraphenoxy-3,4:9,10-perylenediimide

(pH), *N,N'*-dicyclohexyl-1,6,7,12-tetra(*para*-tertbutylphenoxy)-3,4:9,10-perylenediimide (TpH) and *N,N'*-dicyclohexyl-1,6,7,12-tetra(*para*-(1",1",3",3"-tetramethylbutyl)phenoxy)-3,4:9,10-perylenediimide (OpH, Scheme 1), were prepared in order to examine the effect of aromatic group and alkyl chain on gas sensing performance. It was found that the length of alkyl chain on *para*-position of phenoxy unit have remarkable impact on the sensing performance of pH, TpH and OpH by modulating crystalline structure,  $\pi$ - $\pi$  overlap and energy level. It is expected that the detailed analysis of the roles of aromatic groups and alkyl chains will contribute to a better understanding of the structure–property relationship and facilitate the design of PDIs sensing devices.

## 2. Experimental

pH, TpH and OpH were synthesized according to reported procedure with slight modifications [30], and the synthesis procedure was shown in ESI.  $^1\text{H}$  NMR spectra (400 MHz) were recorded on a Bruker ARX 400 with  $\text{CDCl}_3$  or  $\text{CF}_3\text{COOD}$  as the solvent. Elemental analysis was conducted by a Perkin-Elmer 240C Elemental Analyzer. The size and shape of the micro/nanostructure were observed by a field-emission SEM (Hitachi S-4800) operated at an accelerating voltage of 6 kV. The TEM studies were performed using a TECHNAI G2 20 S-TWIN microscope operating at an accelerat-

ing voltage of 120 kV. UV–vis absorption spectra were recorded on Perkin-Elmer Lambda 950 UV–vis spectrophotometer, respectively. The X-ray diffraction patterns of these PDIs micro/nanostructures were performed on a Japan Rigaku D/max-2500 rotation anode X-ray diffractometer, for which a Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) was used. Differential scanning calorimetry (DSC) was performed by using a Perkin-Elmer DSC-10 calorimeter under flowing  $\text{N}_2$  at a heating rate  $10^\circ\text{C}\cdot\text{min}^{-1}$ . The torsion angle was obtained according to a procedure below. Firstly, the most energetically preferable geometry of PDIs is obtained by DFT calculation using DFT/B3LYP program (Fig. S1 in Supplementary information). Then, C1C2C3C4 or C1'C2'C3'C4' dihedral angle, namely, torsion angle, are measured using Gview soft. Cyclic voltammetry was recorded on IM6ex under Ar in dichloromethane solutions with Ag/AgCl as referenced electrode. Valence band ( $E_v$ ) and conduction band ( $E_c$ ) was calculated according to corresponding HOMO and LUMO energies. The LUMO energies for these PDIs were estimated vs vacuum level according to  $E_{\text{LUMO}} = 4.4 \text{ eV} - E_{\text{red1}}$ , and HOMO energies were obtained using the formula  $E_{\text{HOMO}} = E_{\text{LUMO}} - E_g$  from the optical gaps ( $E_g$ ) determined from the overlap of the normalized UV–vis and fluorescence spectra in dichloromethane (Fig. S2 in Supplementary information). Fermi level ( $E_f$ ) was estimated from the average value of  $E_c$  and  $E_v$ .

pH, TpH and OpH devices (Fig. S3 in Supplementary information) were fabricated according to a procedure below. Firstly,  $\text{SiO}_2$ -coated Si (100) substrates were cleaned in a 3:7 mixture of  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$ , rinsed with deionized water, and dried by Ar stream. Then, the micro/nanostructures of pH, TpH and OpH were transferred to substrates in air at room temperature. Finally, drain and source electrodes for current ( $I$ ) – time ( $t$ ) measurement were fabricated by vapor depositing Au ( $2 \times 10^{-6}$  Torr,  $0.5 \text{ \AA/s}$ ,  $\sim 50 \text{ nm}$  thick) onto micro/nanostructure through shadow mask to obtain devices with a channel length of  $50\text{--}100 \text{ }\mu\text{m}$  and width of  $1\text{--}2 \text{ }\mu\text{m}$ . The device was put into the test chamber with a volume of 2 L, which was connected with vacuum with two-way valves. Then a certain amount of hydrazine was injected into the test chamber by a syringe and the variation in current was recorded at room temperature under a fixed voltage of 1 V by a Keithley 4200-SCS system until the current reached a steady value.

## 3. Results and discussion

The micro/nanostructures of pH, TpH and OpH were prepared by precipitation method in chloroform/methanol binary solution ( $0.1 \text{ mg mL}^{-1}$ ) at a volume ratio of 1/4, 1/4 and 1/9, respectively, and the morphologies of micro/nanostructures were characterized by SEM and TEM as illustrated in Fig. 1. SEM and TEM images showed that all of pH, TpH and OpH could well self-assemble into one-dimensional micro/nanostructures, but the detailed morphologies were different. When pH molecules were assembled in chloroform/methanol binary solution, ribbon-like structure with width of  $300\text{--}400 \text{ nm}$  and length up to tens of micrometers were obtained (Fig. 1a, d, Fig. S4a in Supplementary information). Compared with pH, rigid wire-like structures with width of  $300\text{--}400 \text{ nm}$  were obtained for TpH molecules (Fig. 1b, e, Fig. S4b in Supplementary information), with their length up to hundreds of micrometers. Although OpH molecules also self-assembled into ribbon-like structures (Fig. 1c, f, Fig. S4c in Supplementary information), the lengths, with an average of 20 micrometers, were smaller than that of pH and TpH. These results suggested that the length (from 2C to 4C) and branched point (from tertbutyl to 1",1",3",3"-tetramethylbutyl) of alkyl chain can significantly influence aggregated morphologies and crystal structure of PDIs molecules (as discussed below).

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