



Ammonia sensing properties of perylene diimides: Effects of core-substituted chiral groups

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ABSTRACT

The detection of ammonia vapor has strong implications for health, safety and environment. Herein, we reported on an high efficient chemiresistive sensor based on perylenediimide derivatives (PDIs) substituted by (*S*)-1-octyn-3-ol (**SOT**), (*S*)-3-butyn-2-ol (**STB**) and (*S*)-1-phenyl-2-propyn-1-ol (**SPP**) on 1, 7-bay positions. These PDIs devices exhibited high sensitivity, excellent selectivity and low detection limit towards ammonia vapor. In these materials, SPP showed the most efficient sensing performance, and the increment of current is 4 and 1.2 orders of magnitude higher than SOT and STB due to its lowest LUMO energy, uniform and continuous crystalline phase with π - π stacking distance of 3.28 Å. While the highest LUMO energy, poor crystallinity, and smaller π - π overlap as well as largest π - π distance of 3.35 Å resulted in the lowest performance of SOT device. It is expected that excellent sensing parameters and detailed analysis of the roles of core-substituted chiral groups will provide a basis protocol for the design of simple, low-power and high efficient PDIs sensors.

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1. Introduction

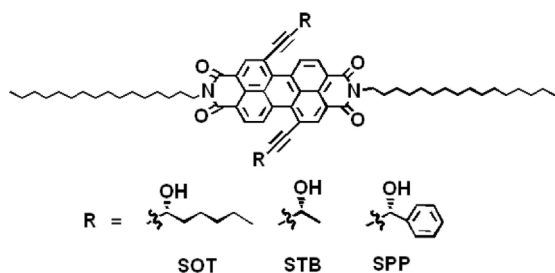
Perylenediimide derivatives (PDIs) are widely applied on optoelectrical devices owing to their better electron acceptor ability with high electron mobility and thermal stability [1–5]. To enhance the performance of PDIs materials, molecular modification is usually considered as one of the most important means. In this regard, introducing of solubilizing substituted groups to PDIs core on the imide N-, bay- and *ortho*-position(s) have been widely utilized [1–5]. 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 [6–8]. In practice, however, the selection of bay substituents has been so far difficult. Because covalently linked bay-substituted groups, such as alkyl, aromatic and heteroaromatic rings, often have complicated effect on coordinated regulation of critical parameters (e.g., crystalline structure, orbital energy levels, π - π stacking and π - π distance) to determine the optoelectrical properties of solid-state materials [9–15]. Therefore, the choice of substituents has

to be carefully thought out to achieve fine balance between these parameters to attain desired electronic properties.

Ammonia (NH₃) is important chemical raw materials that are widespread applications in fertilizers, dyes, drugs, plastics, etc. This gas is highly toxic and corrosive that can be easily spread into the environment, and hence bring severe effect on the safety as well as human health [16–19]. As an *n*-type semiconductors (electron-deficient materials), PDIs have been widely applied as gas sensing devices for the detection of NH₃ and/or amine (electron donor) [20–23]. Recently, many attempts to improve PDIs-based NH₃ sensors have been made. Wei and co-workers developed PDIs single-crystalline micro/nanofibers with a fast response rate, sensitivity of 1%, and long-term stability [24]. Lyer et al. reported that amino-acid-substituted PDIs could detect ammonia at sub-ppm level [25]. Although much success has been achieved for detection of ammonia using PDIs sensing devices, the vapor-based detection of gaseous ammonia still remains challenging, mainly due to the limited availability of PDIs sensory materials that enable vapor detection with high sensitivity and selectivity. Moreover, the relationships between molecular structure of PDIs and their sensing performance need to be further investigated and revealed. To this end, it is highly desirable to design and fabricate new PDI materials with high-performance sensing properties; meanwhile, to scientifically reveal the structure-property relationships.

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Scheme 1. Chemical structure of SOT, STB and SPP.

In recent study, we have demonstrated that stereoisomerism of alkyl chain in the bay regions can well influence PDIs sensing performance in hydrazine vapor. More interesting, chiral perylene showed more enhanced sensing performance compare to their achiral counterparts [26]. These results motivate us to conduct further investigation to reveal that core-substituted chiral groups how to modulate PDIs sensing performance in ammonia vapor. Herein, three chiral perylenediimide derivatives bearing chiral alkyl chain on the 1,7-bay positions, namely, *N, N'*-bis(*n*-dodecyl)-1,7-di((*S*)-1-octyn-3-ol)perylene-3,4:9,10-tetracarboxydiimide (**SOT**) [26], *N, N'*-bis(*n*-dodecyl)-1,7-di((*S*)-3-butyn-2-ol)perylene-3,4:9,10-tetracarboxydiimide (**STB**) and *N, N'*-bis(*n*-dodecyl)-1,7-di((*S*)-1-phenyl-2-propyn-1-ol)-perylene-3,4:9,10-tetracarboxydiimide (**SPP**, Scheme 1) were prepared. Different from our previous report, more emphases in current study are placed on the effect of the length and substituted groups of chiral alkyl chains on the modulating of sensing properties in ammonia vapor. It was found that these PDIs device exhibited high sensitivity, excellent selectivity and low detection limit towards ammonia vapor. While subtle variations in crystalline structure, orbital energy levels, π - π overlap as well as π - π distance that originated from chiral alkyl chain ultimately resulted in their differential response to ammonia vapor. It is expected that excellent sensing parameters and detailed analysis of the roles of core-substituted chiral groups will provide a basis protocol for the design of simple, low-power and high efficient PDIs sensors.

2. Experimental

The synthesis and purification of SOT, STB and SPP were accomplished according to published results with some slight modifications [26], and the detailed synthesis procedure was presented in ESI. ^1H NMR spectra (400 MHz) were measured on AVANCE 400 in CDCl_3 . Elemental analysis was conducted by a Perkin-Elmer 240C Elemental Analyzer. The surface morphologies of spin-coated thin film on glass substrates were observed on a Nanoscope IIIa Atomic Force Microscopy (AFM) in tapping mode. UV-vis absorption spectra were recorded on Perkin-Elmer Lambda 950 UV-vis spectrophotometer. Fluorescence spectra were acquired by using a Perkin-Elmer LS 55 luminescence spectrometer. Circular dichroism (CD) determinations were conducted by a JASCOJ-810 spectrometer at 25 °C. The X-ray diffraction (XRD) patterns of these PDIs films were determined on a Japan Rigaku D/max-2500 rotation anode X-ray diffractometer equipped with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Cyclic voltammetry was conducted on IM6ex under N_2 in dry 0.1 M TBAPF6 in dichloromethane solutions and was referenced to Ag/AgCl . The lowest unoccupied molecular orbital (LUMO) energies for these PDIs were estimated vs vacuum level from $E_{\text{LUMO}} = 4.4 \text{ eV} - E_{\text{red1}}$, and highest occupied molecular orbital (HOMO) energies were estimated 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 PL spectra in dichloromethane (Fig. S1 in ESI).

SOT, STB and SPP devices were fabricated according to a procedure below. Firstly, glass substrates ($1 \times 1 \text{ cm}$) were cleaned in piranha solution, a 7:3 mixture of H_2SO_4 and H_2O_2 , rinsed with deionized water, and dried by N_2 stream. Then, the chloroform solutions ($20 \mu\text{L}$, 1 mg mL^{-1}) of SOT, STB and SPP were spin-coated on the substrates in air at room temperature. Finally, drain and source electrodes were fabricated by vapor depositing Au (2×10^{-6} Torr, 0.5 \AA/s , $\sim 50 \text{ nm}$ thick) onto semiconductor film (ca. 80 nm) through shadow mask to obtain devices with a channel length of $200 \mu\text{m}$ and width of $2000 \mu\text{m}$ (Fig. S2. in ESI).

To evaluate the sensitive characteristics to NH_3 gas, the PDIs devices were stored in a test chamber. High-purity nitrogen (N_2) and 500 ppm standard NH_3 gases were purchased from commercial company, and a mixture with the appropriate concentrations was introduced into the test chamber by a mass flow controller (total flow: $0.4\text{--}0.5 \text{ L min}^{-1}$); the corresponding NH_3 concentration varies ranging from 10 to 100 ppm. During the response process, the sensor is introduced to each concentration of NH_3 for approximately 1–2 min, and during the recovery process, the NH_3 gas is removed, at the same time, nitrogen is continued to introduce until the current recovers to the original value. The concentration of other eight liquid analytes obeys the Formula (1) [25]:

$$C_{\text{ppm}} = (V_{\mu\text{L}} \times D \times T_{\text{surrounding}} \times 2.24 \times 10^6) / (MW_{\text{gas}} \times V_{\text{mL}} \times T_{\text{room}}) \quad (1)$$

where, C_{ppm} is the concentration of analyte vapor, V_{mL} is the volume of the test chamber, $V_{\mu\text{L}}$, D and MW_{gas} is the volume, liquid density (g mL^{-1}) and molecular weight of the liquid analytes (g mol^{-1}). T_{room} and $T_{\text{surrounding}}$ is the room and surrounding temperature (K), respectively. The relative humidity value of 70% was measured at 25 °C on an A210 hygromograph that was supplied by HUATO System Co., Ltd. All electrical characterizations of the devices were carried out using a Keithley 4200-SCS system on bias voltage of 1 V at 25 °C.

3. Result and discussion

As an *n*-type organic semiconductor materials (i.e., electron acceptor), PDIs are capable of acting as sensing materials used to examine some electron donors such as amine [14,20–25]. When PDIs are exposed to amine vapor, the charge transfer interaction took place between PDIs and amine, and PDIs were formed an anionic radical (Fig. S2 in ESI), which provided electrons as the major charge carrier rapidly migrating along π -electron delocalization and ultimately led to increment of current [26,27]. Therefore, the sensing properties of SOT, STB and SPP in different amine gas were firstly investigated on their conductometric gas sensors.

Upon their exposure to ammonia (100 ppm), ethylamine, butylamine, diethylamine, triethylamine, dibutylamine, aniline, 2,4-dimethylaniline and cyclohexylamine (1000 ppm), differential increment of electrical current was achieved (Fig. 1). Compared to other eight amines, SOT, STB and SPP exhibited more remarkable enhancement of electrical current, implying these PDIs materials were more sensitive to ammonia vapor and their outstanding selectivity. The magnitude of ca. 0.009, 0.02 and 0.045 μA was found for SOT, STB and SPP (Fig. 1), suggesting that SPP possess the most excellent sensing performance and the increment of current is 4 and 1.2 times greater than SOT and STB, respectively. Further compared with our previous report (the sensitivity of 40% in ammonia at a concentration of 1% for PTCDI-CN₂C₁₂) [24], these chiral PDIs showed more higher sensitivity, indicating single-handed chirality of PDIs is more conducive to improving their gas sensing performance [28]. Detailed analysis of chemical structure of SOT, STB and SPP, only the chiral alkyl chain in the bay regions is change, imply-

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