Electron-withdrawing groups induced remarkable changes in sensory property based on single micro/nanostructure of perylenediimide derivatives

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HIGHLIGHTS

- PTCDIs micro/nanorods were prepared in chloroform/methanol solutions.
- High sensitivities to hydrazine were found based on PTCDIs gas sensors.
- It showed that core-substituted groups had impact on sensitivity and stability.

GRAPHICAL ABSTRACT
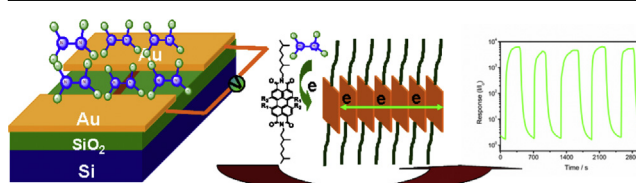
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ABSTRACT

Two perylenediimide derivatives, N, N′-bis(3,7-dimethyloctyl)- 1,7-dicyanoperylene-3,4:9,10-tetracarboxyldiimide and N, N′- bis(3,7-dimethyloctyl)- 1,2,6,7-tetrachloroperylene-3,4:9,10-tetracarboxyldiimide, were prepared and their one-dimensional micro/nanorods were obtained in chloroform/methanol solution. The determination of sensing properties based on their conductometric gas sensors revealed that the increased current was one order of magnitude higher for core-tetrachlorinated perylene than that of core-cyanated one in hydrazine vapor (8 part per million). While better ambient stability in air was found for core-cyanated perylene due to its lower lowest unoccupied molecular orbital (LUMO) energy level and high-ordered arrangement in solid materials. The differential response to hydrazine vapor was less dependent on their surface area and morphologies. It should be ascribed to the difference in activation energy level and twisted skeleton, which are originated from chloride and cyano groups on the bay positions. Discussion for structure-function relationships suggest core-substituted groups have significant impact on the performance of perylene sensing device by modulating band gap and structure of skeleton.

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1. Introduction

Design and development of gas sensors for trace vapor of organic amines represents one of the active research fields in chemistry and materials science, particularly those related to the emerging nanoscience and nanotechnology [1–8]. As an n-type organic semiconductor, perylenetetracarboxylic diimide derivatives (PTCDIs) can be used for probing reducing gases by electrical or fluorescent signals [9]. Recently, different types of PTCDIs gas sensing devices composed of self-assembled nanofiber or nanotube have been developed to detecting volatile amines, among which molecular modification is one of the most important methods to improve the performance of device [9–14]. To date, most modifications of perylenediimide derivatives were achieved by introducing solubilizing substituted groups at the imide nitrogen or adding substituents to the carbocyclic scaffold in the so-

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called bay-area [15–17]. Through latter strategy, some electron-withdrawing groups such as Cl, F and CN can be brought to the conjugated core, which not only change energy level and band gap, but also lead to very large twisting of perylene core so as to significantly affect the performance of sensing devices [18–28]. Since the performance was associated with core substituents, it is expected that some valuable information about structure-function relationships can be unveiled by detailed probing the effect of core-substituted electron-withdrawing groups on the performance of PTCDIs gas sensors.

Ambient stability represents one of the critical parameters that control the performance of organic-based conductometric sensing devices. Because certain species present in ambient air, such as oxygen, can easily diffuse into the semiconductor and destabilize or trap the negative charge carriers in the channel, most n-type organic semiconductor described in the literature so far is the lack of stability under ambient conditions. Although various factors influencing the stability of PTCDIs devices are still a subject of intense research, it is well documented that ambient stability can be achieved by improving solid-state packing modes or reducing their lowest unoccupied molecular orbital (LUMO) energies [15–17]. Concerning PTCDIs gas sensors, although some research works for the effect of substituted groups on their sensing performance have been carried out, the relationship between ambient stability and core substituents still kept veiled until now [22,25,27]. Therefore, some explorations for effect of core-substituted groups on ambient stability need to be conducted to provide guidance for further development of high-stability gas sensor.

In this study, two perylenediimide derivatives: N, N'-bis(3,7-dimethyloctyl)- 1,7-dicyanoperylene-3,4:9,10-tetracarboxyldiimide(PTCDI-CNC$_{10}$), N, N'-bis(3,7-dimethyloctyl)-1,2,6,7-tetrachloroperylene-3,4:9,10-tetracarboxyldiimide (PTCDI-ClC$_{10}$) (Scheme 1) were prepared and their gas response in hydrazine vapor was studied by electricity detection. This work mainly focuses on the effect of electron-withdrawing groups (CN and Cl) on sensing performance of PTCDIs conductometric sensors. It was found that electron-withdrawing groups have significant impact on their response and ambient stability by modulating energy level, band gap and solid-aggregation modes. Detailed analyses of the effect of core-substituted groups on sensing performance were presented.

2. Experimental

The synthesis and purification of PTCDI-CNC$_{10}$ and PTCDI-ClC$_{10}$ were accomplished according to published procedure with slight modifications, and the detailed synthesis procedures were presented in Supplementary Data [22]. ^{1}H NMR spectra (400 MHz) were measured on a AVANCE 400 in CDCl$_3$ with 7.26 ppm as chemical shifts referenced to the internal CHCl$_3$ resonance. The

sizes and shapes of the micro/nanorods were observed by a field-emission SEM (FESEM, 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 accelerating voltage of 120 kV. UV–vis absorption spectra were acquired on a Perkin–Elmer Lamda 950 UV–vis spectrophotometer. Fluorescence spectra were recorded by using a Perkin–Elmer LS 55 luminescence spectrometer. X-ray diffraction measurements were carried out on a Japan Rigaku D/max-2500 rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.54$ Å). The samples for X-ray diffraction measurement were prepared on glass cover slips by drop casting, followed by drying at room temperature. 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 LUMO energies for these PTCDIs in this study were estimated vs vacuum level from $E_{LUMO} = 4.4$ ev − E_{red1}, and highest occupied molecular orbital (HOMO) energies were estimated using the formula $E_{HOMO} = E_{LUMO} - E_g$. The optical gaps ($E_g$) determined from the overlap of the normalized UV–vis and fluorescence spectra in dichloromethane ($\lambda = 529$ nm for PTCDI-CNC$_{10}$ and 530 nm for PTCDI-ClC$_{10}$, Fig. S1 in Supplementary data) according to a semi-empirical equation $E_g = 1240/\lambda$. The gap value of conduction band (E_c) and valence band (E_v) was calculated from respective LUMO and HOMO energy level. Fermi level (E_F) was obtained from the average value of E_c and E_v.

PTCDI-CNC$_{10}$ and PTCDI-ClC$_{10}$ gas sensors were fabricated according to a published procedure with some modifications [28,29]. Firstly, highly doped n-type Si (100) wafers (<0.004 Ω cm) were used as substrates, and a 500 nm SiO$_2$ layer (capacitance per unit area Ci = 7.5 nF cm^{-2}) as a gate dielectric was thermally grown onto the Si substrates. These wafers were cleaned in piranha solution, a 7:3 mixture of H$_2$SO$_4$ and H$_2$O$_2$, rinsed with deionized water, and then dried by N$_2$ stream. Then, self-assembled PTCDI-CNC$_{10}$ and PTCDI-ClC$_{10}$ micro/nanorods in chloroform/methanol were transferred to Si/SiO$_2$ substrates by drop-casting, followed drying in air, and a single micro/nanorod as sensitive layer was obtained. Finally, drain and source electrodes for current(I)−time(t) measurement were fabricated by vapor depositing Au (5 × 10^{-5} Torr, 0.5 Å/s, ~50 nm thick) onto semiconductor micro/nanorods with a shadow mask to obtain devices with a channel width of 0.2−0.6 μm and length of 5 mm. The device was put into the test chamber having a volume of 2 L, which was connected with vacuum with two-way valves. The current variations were recorded at 25 °C in vacuum with a Keithley 4200-SCS system until the current reached a steady value. Then a certain amount of hydrazine was injected into the test chamber. The response was defined as the ratio of I/I$_0$, where I and I$_0$ represented the current flowing through single micro/nanorod on exposure to hydrazine vapor and in vacuum, respectively.

3. Results and discussion

The micro/nanostructure of PTCDI-CNC$_{10}$ and PTCDI-ClC$_{10}$ was prepared according to published procedure with slight modifications in a chloroform/methanol mixed solvents (0.1 mg mL^{-1}) at a volume ratio 2/3 and 1/6, respectively [23]. As shown in Fig. 1, SEM and TEM images showed PTCDI-CNC$_{10}$ and PTCDI-ClC$_{10}$ molecules could well self-assemble into one-dimensional micro/nanorod, but the detailed morphology was different. When PTCDI-CNC$_{10}$ molecules were aggregated in chloroform/methanol solution, ultralong rod-like structure (Fig. 1a, b) with lengths up to several millimetres and an average width of 200−500 nm were obtained. Compared with PTCDI-CNC$_{10}$, micro/nanorods with a similar diameter were also obtained for PTCDI-ClC$_{10}$ molecules (Fig. 1c, d), but the length was decreased to tens of micrometers. To further clarify the crystal structure of these microrods, selective-area electron diffraction
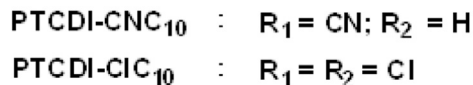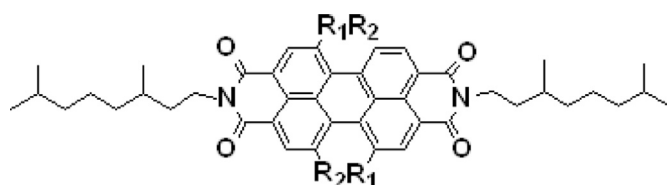
Scheme 1. Molecular structures of PTCDI-CNC$_{10}$ and PTCDI-ClC$_{10}$.

PTCDI-CNC$_{10}$: R$_1$ = CN: R$_2$ = H

PTCDI-ClC$_{10}$: R$_1$ = R$_2$ = Cl