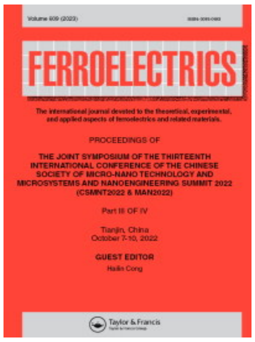

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Study on the self-assembly performance of a perylene derivative

Hong Wei[a#], Li Wen-jie[c,d#], Yang Jianlin[a], Shen Ding[a], Yang Shaobin[a], Jiao Tifeng[b], Wang Ming[a], Zhuang Yongjian[e], and Ma Jifeng[e]

[a]Key Laboratory of Mineral High Value Conversion and Energy Storage Materials of Liaoning Province, College of Materials Science and Engineering, Liaoning Technical University, Fuxin, P. R. China; [b]State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao, P. R. China; [c]Technology center of Shijiazhuang customs district, Shijiazhuang, P. R. China; [d]Tangshan Customs Comprehensive Technical Service Center, Thangshan, P. R. China; [e]Xuzhou Mito Instrument Equipment Co., Ltd, Xuzhou P. R. China

ABSTRACT
Perylene diimide (PBI) had high thermal stability and solubility, so it could be used as a practical new type material of energy saving and environmental protection. The solubilization and photoelectrical properties of the bays can be effectively improved by introducing substituents in the bays. On the other hand, the imide group has a strong ability to absorb electrons, and the alkoxy group after the bay site substitution makes it easy to form micro-nano fiber in good and bad solvents. In other words, most of the properties of PBI derivatives are related to their ability to form micro-nano fiber. A systematic study of N, N′ -isoctyl-1, 7-bis (octanoxy) perylene diimide (DFPBI) was carried out by UV-VIS spectrophotometry, thermogravimetry and fluorescence spectrophotometry. A number of test results show that DFPBI has better solubility and thermal stability than PBI, and can grow micro-nano fiber in both good and bad solvent systems. Therefore, DFPBI has broad application prospects in sensors.

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KEYWORDS
Perylene diimide; derivatives; absorption spectrum; photoelectric performance; micro-nano fiber

1. Introduction

Supramolecular self-assembly generally refers to the process in which more than one molecule spontaneously forms aggregates with specific structures and functions under the influence of non-covalent bonding, such as hydrophobic effect, π-π stacking and hydrogen bonding. Among them, the synergistic effect of various non-covalent bonds drives the formation of supramolecular systems with specific structures, and further maintains the stability and integrity of the system structure [1]. By studying the unique physicochemical phenomena in supramolecular systems at mesoscopic scale, researchers have realized the regulation of the structure and function of supramolecular systems and applied them to functional gel systems, molecular probes, molecular machines, organic micro-nano optoelectronic devices and other fields [2–5]. Nowadays, with the cross of chemistry, biology, materials, information and other disciplines, supramolecular

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CONTACT Wei Hong ✉ lgdhongwei@qq.com; Tifeng Jiao ✉ tfjiao@ysu.edu.cn; Ming Wang ✉ mwang_neu@126.com
[#]Hongwei and Li Wenjie are co-first authors of the article.

self-assembly has gradually developed into a cutting-edge discipline with great application potential – supramolecular science.

Perylene diimide (PBI) can be seen as two naphthalene molecular units bonded by SP2 hybrid orbitals to form a large planar aromatic system. The introduction of substituents in the bay position and imide position of PBI can improve the solubility and photoelectric properties [6]. The introduction of flexible groups such as long alkyl chains on the nitrogen atom (-N) of imide can improve its solubility, and the introduction of alkyl chains can also change the specific optical properties of such compounds, so that the molecules can expand absorption to a wider absorption range and a lower absorption band gap [7]. The planarity of perylene core was destroyed by introducing substituents to chlorine or bromo atoms in the bay site, which led to the increase of molecular packing interval in the crystal, and then the intercovering degree of perylene core was decreased. Thus, the intermolecular large π bond of perylene imide derivatives was weakened or disappeared, and the lattice energy of perylene imide derivatives was also decreased accordingly. The introduction of electron donor substituents at positions 1, 7 or 1 and 6 of the parent perylene ring greatly changed the maximum absorption and emission spectra of perylene imide compounds, resulting in a red shift and a significant decrease in fluorescence quantum yield [8, 9]. The reason is that the large plane of perylene ring is an electron-deficient system, and when electrons are injected into it, the energy difference between the HOMO and LUMO of perylene ring decreases due to the electron absorption effect of the four carbonyl groups at the parent ends of the perylene ring, thus causing the corresponding spectral red shift.

PBI is an environmentally friendly, energy-saving, practical and excellent photoelectric material. Experiments found that N, N' -isoctyl-1, 7-bis (octanoxy) perylene diimide (DFPBI) had better solubility and thermal stability, wider absorption range and lower absorption band gap, and the phenomenon of micro-nano fiber growing in good and bad solvents. Further study of the properties of micro-nano fiber and their application in the field of color change can make up for the shortcomings of other materials in the performance of color change devices.

2. Experiment

2.1. Reagents and instruments

DFPBI and DBPBI (N, N'-isoctyl perylene diimide) were synthesized in the laboratory. Dichloromethane, methanol and other reagents were analytically pure.

Comprehensive thermal analyzer STA449C; Lambda 650 UV-VIS spectrometer, LS45 fluorescence spectrometer; CHI650D electrochemical workstation; Scanning electron microscope.

2.2. Experiment

The dichloromethane solution of DFPBI with a concentration of 10–3mol/L was prepared. Methanol was added at a ratio of 1:9 (1 part dichloromethane and 9 parts methanol). The solution was allowed to stand for a week and the precipitate was taken for scanning image.

3. Results and discussion

3.1. Basic structure and thermal properties

Fig. 1(b) shows the structural formulas of DBPBI and DFPBI. DBPBI introduces a long alkyl chain -isooctyl amine into the nitrogen atom (-N) of imide, and DFPBI introduces alkoxy group into the bine site, which effectively improves its solubility in dichloromethane and other organic solvents. TG and TGA curves show that DBPBI (solid line) starts to decompose near 220 °C DFPBI (dashed line) is significantly more stable than DBPBI, and does not begin to decompose until about 350 °C.

3.2. UV-VIS absorption spectra and fluorescence spectra

DFPBI was obtained by replacing the electron donor group (alkoxy group) of DBPBI at the bay site, which greatly changed the positions of the maximum absorption and emission peaks of perylene imide compounds, so that the absorption range of UV spectrum became wider and the absorption band gap of perylene imide became lower.

DBPBI and DFPBI were prepared into dichloromethane solution at a concentration of 2 × 10–5mol/L. The characteristic absorption peaks of DBPBI are at 525 nm and 488 nm, and those of DFPBI are at 537 nm and 503 nm, which are mainly generated by π-π^* transition of electrons. The reason for this is that the large plane system of the perylene ring is electron deficient, and the substituents belong to electron donor groups. When the injection electronic, due to the four carbonyl) rings at the ends of the matrix with electron-withdrawing effect, this makes the molecules of the highest occupied orbital (HOMO) and the lowest not possess rail (LUMO) is reduced, the energy difference between to a larger degree of change) imide compounds of maximum absorption and emission spectrum, make its redshift, and has a wider range of absorption, Better optical performance (see Fig. 2).

The maximum characteristic absorption peak (537 nm) of DFPBI was used for excitation. A fluorescence characteristic emission peak appeared at 593 nm, and the introduction of bay methyl phenoxy group made the fluorescence characteristic peak red shift. The peak shape of the excitation spectrum emitted at 593 nm is similar to that of the

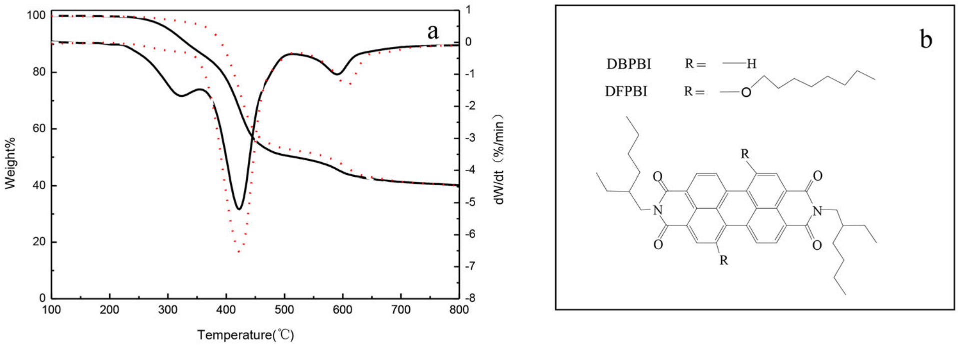

Figure 1. TG curves and molecular structures of DBPBI and DFPBI. (a) The curves of TG (DBPBI – solid line, DFPBI – dashed line); (b) the schematic diagram of molecular structure of DBPBI and DFPBI).

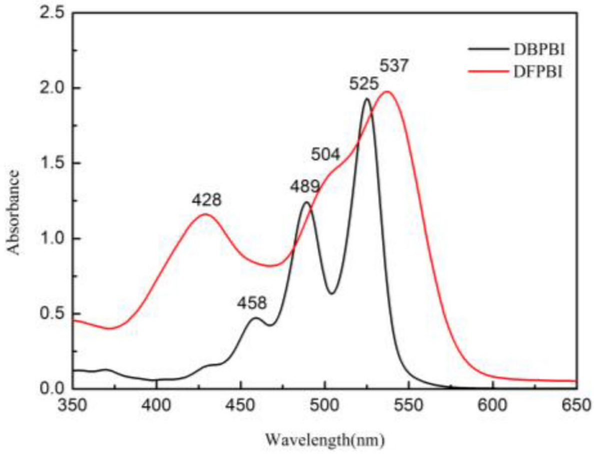

Figure 2. The absorbance spectrums of DBPBI (black) and DFPBI (red).

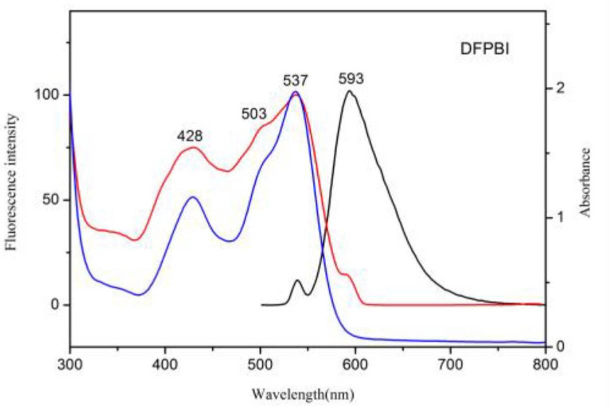

Figure 3. The absorbance spectrum (blue) and fluorescence spectrum (black and red).

absorption spectrum, and is mirror symmetric to that of the fluorescence spectrum (as shown in Fig. 3).

3.3. Electrochemical test

DFPBI was prepared into 5 × 10–4mol/L dichloromethane solution with 0.1 mol/L tetrabutyl hexafluorophosphatium as electrolyte, and the cyclic voltammetry curve was measured at room temperature after deoxygenation with nitrogen. Ag/Ag + was used as the reference electrode, and ferrocene was used as the internal standard [10].

Fig. 4 shows the cyclic voltammetry curve of DFPBI. The HOMO and LUMO of DFPBI can be calculated as −6.79 eV and −4.54 eV according to the formula ELUMO = −([Eonset] red + 4.8 eV)18 and EHOMO = Egopt + ELUMO. According to literature reports, the HOMO and LUMO of P3HT (poly3-hexylthiophene) are 5.1 eV and 3.2 eV, indicating that DFPBI effectively drives exciton separation at the

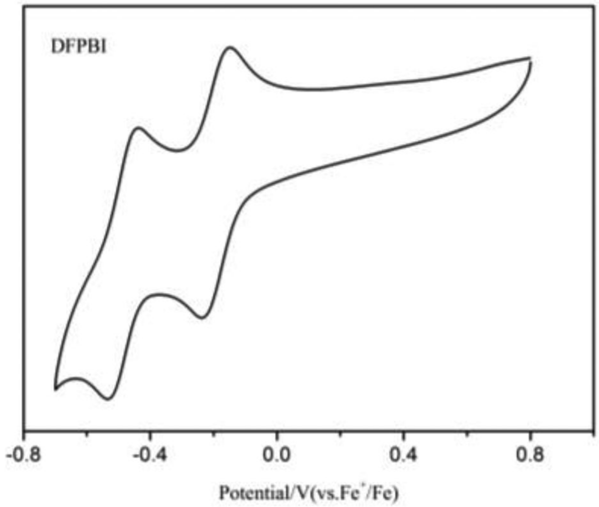

Figure 4. Cyclic voltammetry curves of DFPBI in DMF solution

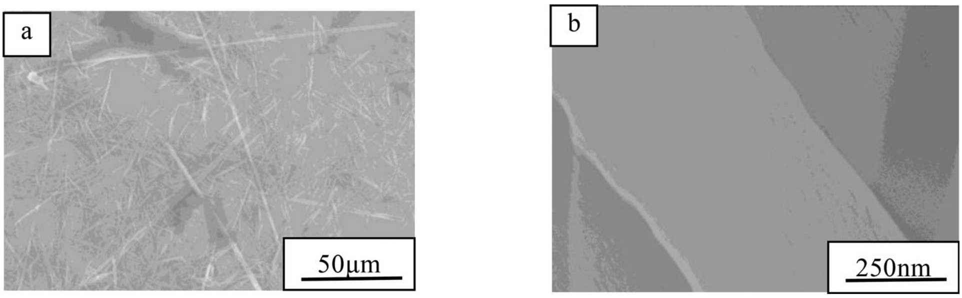

Figure 5. The SEM of DFPBI micro-nano fiber.

heterogeneous interface of P3HT/PDI. Therefore, DFPBI is suitable to be an electron acceptor in P3HT/PBI system.

3.4. Study on properties of micro-nano fiber

The rod-like micro-nanofibers of DFPBI were obtained according to the method described in 1.2. Fig. 5 is the SEM image of DFPBI nanostructure, from which it can be observed that DFPBI molecules are arranged along the one-dimensional direction to obtain the micro-nano structure. The length of the nanorods structure is about tens of microns, and the width is about 0.5 microns. In the SEM figure, it can be seen that the morphology of the nanorods is like a cuboid with a rod-like structure with slight bending. This may be because this nanostructure is mainly assembled through intermolecular π-π interaction and hydrophobic interaction. The intermolecular forces in the nanostructure of DFPBI are shown in the following figure. This bending may be caused by the twisting of molecular aggregation in PITD during self-assembly.

4. Conclusion

PBI is an excellent photoelectric material with high solubility, good stability and strong photoelectric performance. The thermal stability, solubility, absorption range, characteristic peak of UV-VIS absorption spectrum and emission characteristic peak of fluorescence spectrum were improved by the substitution of bay alkoxy group. The π-π interaction in good and bad solvents and the formation of hydrophilic and hydrophobic self-assembly of micro-nanofibers indicate their potential applications in color-changing devices and sensing.

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