



# Bulky rigid substitutions: A route to high electron mobility and high solid-state luminescence efficiency of perylene diimide



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## ABSTRACT

In this paper, we report that a kind of perylene diimide derivative with bulky rigid substituents, 1,7-bis(*p*-tert-butylphenoxy)-*N,N'*-dicyclohexyl-perylene-3,4,9,10-tetracarboxylic diimide (TBPCHPDI) possesses both high electron mobility ( $1.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) and high fluorescence quantum yield (0.32) in the solid state. Through X-ray diffraction (XRD), UV–Vis absorption and fluorescence spectra, and differential scanning calorimetry (DSC) measurements, it is demonstrated that the above phenomenon can be ascribed to the unique crystal structure of TBPCHPDI: due to steric hindrance of bulky rigid substituents, the intermolecular  $\pi$ – $\pi$  actions are neglectable, providing high luminescence efficiency; in the mean time, the spacing between perylene chromophores is still very short (3.47 Å), which is favorable for the hopping transportation of charge carrier from one molecule to neighboring molecule. Therefore, our finding would help design and synthesize novel organic semiconductive materials with potential applications in electrically pumped lasers which require high emission efficiency when large current density is applied.

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## 1. Introduction

Compared to inorganic semiconductors, soluble organic semiconductive materials, including small molecules and polymers, show particular advantages because they can be fabricated into large-area, flexible electronic and opto-electronic devices (organic light-emitting diodes [1,2], thin-film transistors [3–8], and solar cells [9–14], etc.) by low-cost solution-processing. To assure good solubility, it is necessary to introduce soluble groups into organic semiconductive molecules. Poly(3-hexylthiophene) (P3HT) is a typical example [3]. Alkyl side chain is selected as the soluble group because of its flexibility and small steric hindrance, which has a minor effect on

intermolecular approaching and strong  $\pi$ – $\pi$  stacking of organic semiconductive molecules; in some cases, alkyl groups even facilitate the self-assembly of organic semiconductive molecules into ordered structure through interdigitated actions [3]. Consequently, organic semiconductive molecules with flexible linear side chains, such as alkyl and fluoroalkyl, usually own high charge carrier mobility, which is a prerequisite for efficient organic electronic and opto-electronic devices.

On the other hand, isolated organic semiconducting molecules, e.g. present in diluted solution, possess high photoluminescence quantum yield. Nevertheless, once they aggregate into condensed phase, in most cases, their fluorescence quenches tremulously due to dipole–dipole interactions, which originates from parallel packing of adjacent molecules (H-aggregates) [2]. Therefore, the trade-off between high solid-state luminescence efficiency and good charge-transporting ability embedded in single organic semiconductive material has limited its

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widespread deployment in the field of organic optoelectronics, especially in the electrically pumped lasers where large current density is required [15].

Perylene diimide (PDI) is a typical kind of *n*-type semiconductive molecule with excellent electronic and opto-electronic properties. Due to planar molecular geometry, PDIs with linear alkyl or fluoroalkyl substituents normally stack cofacially and form H-aggregates, providing a high electron mobility [16–19] but a low solid-state luminescence efficiency, which can be ascribed to the formed excimeric trap state in the aggregates [20]. Until now, remarkable electron mobility as high as  $6\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  from the single crystal of a core-cyanated perylene diimide derivative with fluoroalkyl substitutions at *N*-atoms (PDIF-CN<sub>2</sub>) has been reported [18]. In contrast, for the applications in field of luminescence, PDIs must be modified with bulky substituents, such as branched alkyls, cyclic alkyls, and aryls, in order to keep the molecule far away from neighboring molecules in the solid state because of twisted molecular geometry [21–24]. For example, Che et al. found that a PDI modified with cyclohexyl substituents shows strong fluorescence emission, which can be attributed to flip-flap crystalline stacking afforded by the specific side chains [24]. However, to our best knowledge, no PDIs possessing both high electron mobility and high solid-state luminescence efficiency have been reported.

Taking the above into account, in this work, we investigated the charge-transporting and solid-state luminescence performances of a kind of perylene diimide derivative with bulky rigid substituents (two *p*-tert-butylphenyl groups and two cyclohexyl groups), 1,7-bis(*p*-tert-butylphenoxy)-*N,N'*-dicyclohexyl-perylene-3,4,9,10-tetracarboxylic diimide (TBPCHPDI), which was reported firstly by Feng et al. [23]. The effects of bulky rigid substituents on the electron mobility and solid-state luminescence efficiency of perylene diimide were studied. Through the analysis of the crystal structure of TBPCHPDI, the effect of bulky rigid substituents on the electronic and optical properties of perylene diimide was investigated, in order to explore a feasible route to organic materials with both excellent charge-transporting and good light-emitting capabilities.

## 2. Experimental section

### 2.1. Materials and equipments

All chemical reagents were purchased from Acros Organics Co., and were used as received. Solvents (A.R.) were commercially available, and were purified through conventional procedures prior to use. NMR spectra were obtained on a Bruker DMX400 (400 MHz) nuclear resonance spectroscope. Mass spectra were performed on a Waters Maldi Q-TOF Premier mass spectroscope. UV-Vis spectra were taken on a Varian CARY100 Bio spectrometer. Fluorescence spectra and fluorescence quantum yield were recorded on a HORIBA Jobin Yvon FluoroMax-4 fluorescence spectrophotometer equipped with an integrating sphere. DSC curves were measured on a Perkin-Elmer Pyris

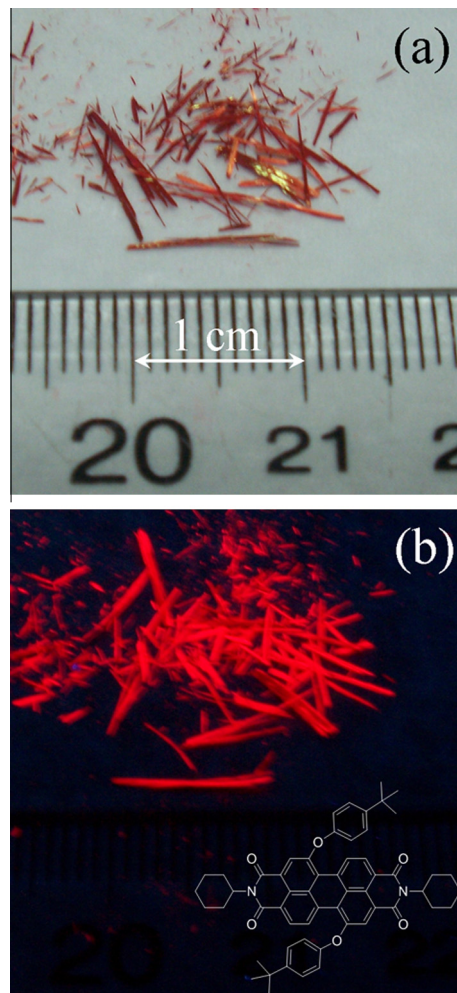
1 differential scanning calorimeter. X-ray diffraction (XRD) measurements of single crystal were performed on a Rigaku R-Axis RAPID X-ray diffractometer.

### 2.2. Synthesis of TBPCHPDI

TBPCHPDI was prepared according to the synthetic procedure reported before [23]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ/ppm): δ = 9.48 (d, *J* = 8.4 Hz, 2H), 8.49 (d, *J* = 8.4 Hz, 2H), 8.24 (s, 2H), 7.46 (d, *J* = 8.7 Hz, 4H), 7.07 (d, *J* = 8.7 Hz, 4H), 4.94–5.02 (m, 2H), 2.46–2.57 (m, 4H), 1.20–1.91 (m, 16H), 1.37 (s, 18H). Maldi-TOF-MS: *m/z* 850.6.

### 2.3. Growth of TBPCHPDI crystals

~20 mg TBPCHPDI was soluble in 1 ml CHCl<sub>3</sub>. After the solvent was evaporated very slowly (~3 days) and completely at room temperature, needle red TBPCHPDI crystals were obtained.



**Fig. 1.** The photographs of TBPCHPDI crystals under day light (a) and upon illumination with UV light. (b) The inset is the molecular structure of TBPCHPDI.

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