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Review

Cation-induced self-assembly of an amphiphilic perylene diimide derivative in solution and Langmuir–Blodgett films

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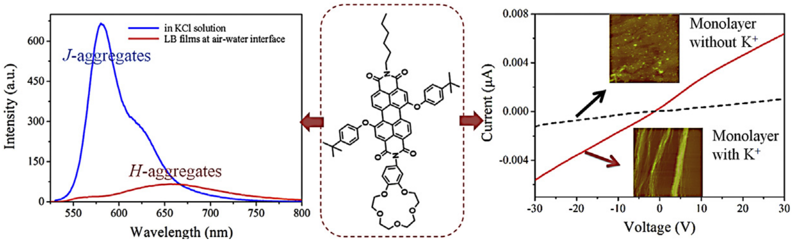
HIGHLIGHTS

- A new amphiphilic, unsymmetrical 15C5PDI compound was synthesized.
- Cation-induced aggregation from J-type into H-type was obtained.
- Fluorescence emission change from "switch-on" to "switch-off" is observed.
- Nanostructures formed at various air/liquid interface with different morphology.
- A significantly enhanced conductivity was obtained from 1D nanofibrils of 15C5PDI.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel amphiphilic perylenetetracarboxylic diimide (PDI) derivative, N-(4′-benzo-15-crown-5-ether)-N-hexyl-1,7-di(4-tert-butyl-phenoxy)perylen-3,4,9,10-tetracarboxylic diimide (15C5PDI), has been synthesized and characterized. Dimerization of 15C5PDI is induced in $CHCl_3$ solution with the present of K^+, resulting in the formation of the slipped co-facial *J*-aggregates, as revealed by absorption and fluorescence spectroscopies. Analysis of the surface pressure–area (π–A) isotherms and spectral change for the monolayer formed at the air/water interface, disclosed that 15C5PDI molecules adopted the *H*-type aggregation mode with a face-to-face configuration and edge-on orientation on both the surface of pure water and K^+ aqueous solution. Consequently, a particularly interesting fluorescence emission change from "switch-on" to "switch-off" could be observed upon aggregation that was accompanied by a transformation from strongly fluorescent *J*-type into non-fluorescent *H*-type packing of the 15C5PDI dyes. Depending mainly on the coordination bonding between 15-crown-5-ether groups and K^+ ions, one dimensional nanofibrils formed on the surface of the K^+ aqueous solution with a more closely arrangement of 15C5PDI molecules relative to those on pure water subphase revealed by the π–A isotherms and atomic force microscopy (AFM) images. X-ray diffraction studies indicate that the film crystallinity and general molecular order in the Langmuir–Blodgett (LB) films deposited from the KCl solution are improved effectively in comparison with those from pure water subphase. Furthermore, the conductivity of the LB films prepared in K^+ solution is more than ca. 1 order of magnitude higher than those from water.

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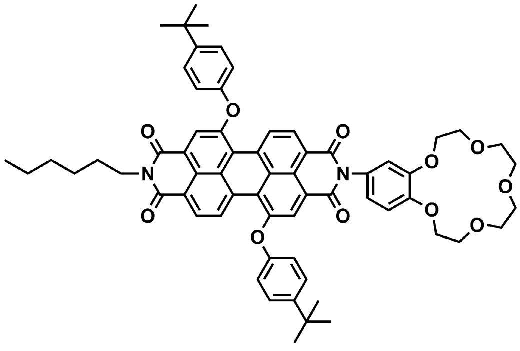
Contents

1. Introduction

The construction of nano-structures with controlled morphology for π-conjugated organic molecules and programming supramolecular interaction have received increasing research interests due to the technical requirements for the development of efficient electronic and optoelectronic devices [1–3]. The major driving force operating in these precisely controlled nanoscopic architectures arises from various non-covalent interactions including π–π interaction, van der Waals forces, hydrogen bonding, hydrophilic/hydrophobic interactions, electrostatic and metal–ligand coordination. As a result, comprehensive understanding the interplay among these factors in both solution and the thin solid films to finely tune the packing model of organic molecules has formed the focus of current research interests in this field [4–6]. As an important functional dye with outstanding photo and chemical stability as well as interesting photophysical and photochemical properties, perylenetetracarboxylic diimide derivatives (PDIs) have been intensively studied as advanced molecular materials for sensors [7], organic solar cell [8] and organic field-effect transistors (OFETs) applications [9–11]. Considerable efforts have been devoted to correlating the relationship between the π-orbital overlap among neighboring conjugated molecules and carrier transport properties aiming for improving their performance [12–16]. For instance, substituents were incorporated to pentacene molecules to prevent C—H···π forces and induce more effective π–π interactions between pentacence molecules, thus leading to improved OFET properties [17–20]. Very recently, we have designed and prepared a cyclophane of perylene tetracarboxylic diimide (PDI) with four phenoxy substituents at the bay positions of the two PDI rings, which were revealed to show unexpectedly good n-type OFET properties and device environmental stability resulting from the formation of intra- and inter-molecular *H*-aggregates associated with the segregation effects imparted by the flexible hydrophobic alkyl substituents at the imide nitrogens of the PDI molecule [21,22]. It is worth noting that a significant effort has been made toward self-assembly of symmetrical PDI derivatives into one-dimentional (1D) nanostructures including nanobelts [23,24], nanotubes [25,26] and nanofibers [27,10]. Depending mainly on intermolecular π–π stacking, the 1D alignment of π-conjugated molecules facilitates carrier transport, which enables their applications in optoelectronic devices. We have also designed and prepared a series of symmetrical PDI derivatives, and found that the nanostructural morphology was affected by both molecular modification and the solvent effect [28,29,9,30–32]. Langmuir and Langmuir–Blodgett (LB) techniques are useful tools to fabricate monolayer and/or multilayer films with controllable structure and molecular orientations in the molecular level [33]. However, the application of LB techniques in the construction of nanostructure for unsymmetrical PDI derivative having the different hydrophobic/hydrophilic substituents is scarcely reported so far probably because of the difficulties on the synthesis of unsymmetrical, amphiphilic PDIs [34]. For the purpose of extensive studies, we describe herein the synthesis and characteristics of a new unsymmetrical, amphiphilic perylenetetracarboxylic diimide (PDI) derivative with a hydrophilic 4-benzo-15-crown-5-ether unit and a hydrophobic alkyl chain linked at the imide nitrogen positions, named as N-(4′-benzo-15-crown-5-ether)-N-hexyl-1,7-di(4-tert-butyl-phenoxy)perylen-3,4,9,10-tetracarboxylic diimide (15C5PDI), Scheme 1. The introduction of functional crown ether group having remarkable recognition and metal binding ability at the one side of imide nitrogen position on the PDI ring make it possible to tune molecular packing mode by cation-induced self-assembly, while hydrophobic linear alkyl chain linked at the another side of imide nitrogen position is to expected to provide sufficient flexibility for the optimization of the noncovalent stacking of the perylene diimide π systems. We show that this amphiphilic molecule self-assembled into a dimeric double-decker structure in solution and 1D nanofibrils formed from complementary coordination between crown ether and alkali ions at an air/water interface. In addition, the significantly improved semiconducting properties of the nanostructures fabricated from 15C5PDI in the presence of potassium ions relative to these in the absence of potassium ions, are also revealed by *I*–*V* measurements.



Scheme 1. The molecular structure of 15C5PDI.

2. Experimental

2.1. Chemicals

4-Aminobenzo-15-crown-5-ether was purchased from Tokyo Chemical Industry Co., Ltd. All other reagents and solvents were