



Optical properties and structural morphology of one-dimensional perylenediimide derivatives

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ABSTRACT

Three derivatives of perylene diimide, namely *N,N'*-ditridecylperylene-3,4,9,10-tetracarboxylic diimide (DT-PDI), *N,N'*-dipentylperylene-3,4,9,10-tetracarboxylic diimide (DP-PDI) and *N,N'*-bis(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic diimide (DH-PDI) differ in their side-chain substitution have been examined to study the effect of side-chain substituents on their optical properties and structural morphology. Due to the different side-chain, the self-assembly of these molecules results in totally different optical properties and structural morphologies, as confirmed from the steady-state absorption and fluorescence, time resolved fluorescence, and scanning electron microscopy (SEM) techniques. The collected results confirmed the formation of one-dimensional (1D) nanowires in the case of short linear side chain, chunky aggregates in the case of long linear substituted side chain, and zero-dimensional (0D) nanospheres with the branched substituted side chain.

1. Introduction

Recently, developing renewable energy sources has stimulated tremendous interest in construction of light energy conversion systems [1–5]. For this purpose, several light harvesting materials, which have ability to convert the light energy into chemical energy, have been reported in the last decades [6–12]. Among them, perylene tetracarboxylic diimide (PDI) dyes are promising materials for the light based applications due to their large planar π -systems, strong absorption in the visible region, high photoemission, high electron deficiency, as well as high chemical persistency, thermal durability, and photostability [13–20]. Because of the planar structure and peripherally rich oxygen atoms, perylene dyes favor π - π stacking between the layer-stacked molecules, which creates a basis of well-defined growth. Substitution at the imide and bay positions of the perylenediimide can make significant effect on the solubility variations, optical and electrochemical properties, and the structural morphology [21–25].

In continuous to our efforts to examine the photophysical and photochemical behavior of the perylenediimide derivatives [26–33], we examined herein the self-assembly of three perylene derivatives differ in their side-chains at the imide positions, namely *N,N'*-ditridecylperylene-3,4,9,10-tetracarboxylic diimide (DT-PDI), *N,N'*-dipentylperylene-3,4,9,10-tetracarboxylic diimide (DP-PDI) and *N,N'*-bis(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic diimide (DH-PDI). As seen from Fig. 1, DH-PDI is substituted with a branched alkyl chain, whereas DP-PDI and DT-PDI were substituted with short and long

linear alkyl chain, respectively.

To explore the effect of side-chain substituents on the optical properties and structural morphology of the examined PDI derivatives, the steady-state absorption and emission, and time-correlated singlet photon counting techniques have been utilized in different solvents. The structural morphology has been also examined by using the scanning electron microscopy (SEM).

2. Experimental section

N,N'-ditridecylperylene-3,4,9,10-tetracarboxylic diimide (DT-PDI), *N,N'*-dipentylperylene-3,4,9,10-tetracarboxylic diimide (DP-PDI) and *N,N'*-bis(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic diimide (DH-PDI) were purchased from Aldrich and used as received. The utilized organic solvents were purchased from Aldrich and used without any further purification. Ultrapure water was generated with Milli-Q apparatus (Millipore).

Optical absorption and fluorescence measurements were carried out on a JASCO spectrophotometer (V-780) and a JASCO spectrofluorometer (model FP-8300), respectively. The picosecond fluorescence decay profiles were measured by a single-photon counting method using FluoTime 300 (PicoQuant, Germany). Lifetimes were evaluated with software attached to the equipment. Scanning electron microscopy (SEM) images of nanowires and nanospheres were recorded on a JEOL FE-SEM JSM-6320F instrument. SEM samples were placed on a piece of glass that was attached to gold metal.

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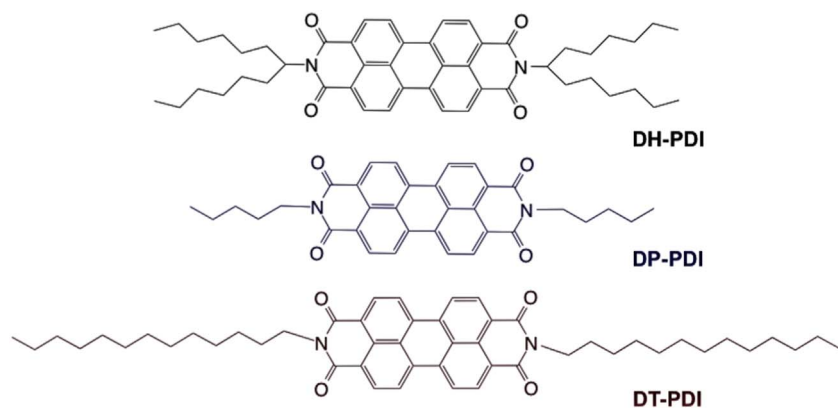


Fig. 1. Molecular structures of the examined PDI derivatives.

3. Results and discussion

3.1. Absorption and fluorescence studies

3.1.1. DP-PDI

As shown in Fig. 2, the absorption spectrum of DP-PDI in chloroform exhibited three characteristic absorption bands at 527, 490, and 458 nm corresponds to 0–0, 0–1 and 0–2 electronic transitions, respectively. The same features were observed in dimethylformamide (DMF), toluene (TN) and tetrahydrofuran (THF) (Table 1). This observation suggests the formation of the monomer form of DP-PDI in these solvents [26–33]. When changing the solvent to methanol (MeOH), acetonitrile (ACN) and hexane, an enhancement of 0–1, 0–2 and 0–3 electronic transitions was observed compared to 0–0 electronic transition, in addition to the appearance of a new absorption band at 580 nm. These optical observations in methanol, acetonitrile and hexane suggested a strong π - π interaction in co-facial form of molecular stacking [34–37].

Upon excitation of DP-PDI with 470 nm light, the emission spectrum in chloroform exhibited emission peaks at 537, 576 and 625 nm (Fig. 2, right). Similar emission observations were recorded for DP-PDI in DMF, THF and TN, suggesting the existence of DP-PDI in the monomer form in these solvents. When changing the solvent to methanol, acetonitrile and hexane, the fluorescence bands were heavily

quenched, suggesting the existence of DP-PDI molecules in the aggregated forms. With the comparison of the monomer form in THF, it was found that the percentage of molecules transformed into the aggregated form in MeOH reached 96.1%. Upon exciting the DP-PDI with 580 nm light, it was found that the DP-PDI exhibited almost no emission bands because of the symmetry forbidden transition involving lower energy of π -stacking state.

The fluorescence lifetime measurements of DP-PDI tracked those of the steady state fluorescence measurements. Fig. 3 shows the fluorescence decay profiles in different organic solvents by using 470 excitation-light. By fitting the decay profiles with a single exponential decay, the fluorescence lifetimes were determined to be 4.68, 4.63, 4.60, and 4.46 ns in toluene, dimethylformamide, chloroform, and tetrahydrofuran, respectively. On the other hand, the measurements showed considerably short fluorescence lifetimes in the case of methanol (4.21 ns), acetonitrile (4.16 ns), and hexane (3.86 ns). From these values, it is obvious that the fluorescence lifetimes of DP-PDI in the monomer form are considerably longer compared to the aggregated form (Supporting information, Fig. S1).

3.1.2. DT-PDI

The absorption spectra of DT-PDI (with long alkyl chain at the imide positions) showed the same absorption features as that for DP-PDI. As shown in Fig. 4 and Table 1, DT-PDI exists in its monomer form

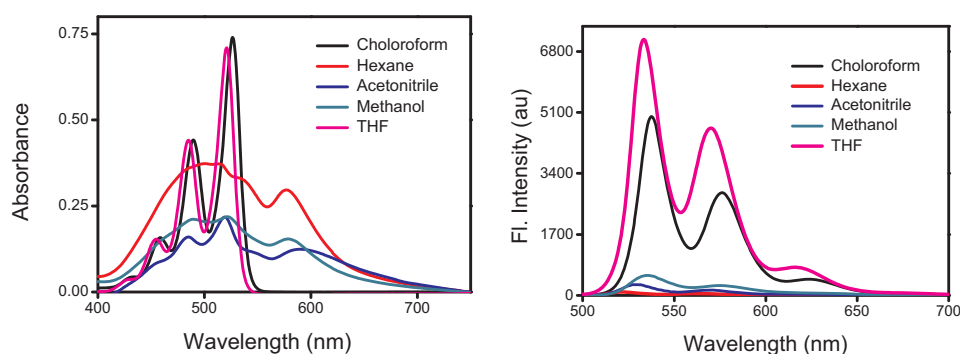
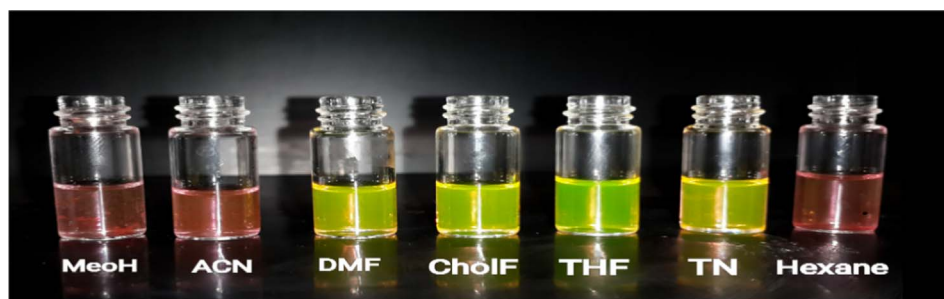


Fig. 2. Absorption (left) and fluorescence spectra (right) of DP-PDI in the indicated solvents. (Bottom) The color of fluorescence emission of DP-PDI is tuned in the examined organic solvents.



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