



The influence of substituents of perylenediimides on their spectroscopic properties



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ABSTRACT

The influence of substituents of newly synthesized perylenediimides on their spectral properties and excited state relaxation has been studied by means of steady-state and time-resolved spectroscopy and quantum chemical calculations. Substituents at the perylene core cause broadening and shift of the absorption and fluorescence bands and also reduce the fluorescence quantum yield. Organic 4-tert-butylphenoxy substituents reduce the fluorescence yield by tens of percent by slightly reducing the oscillator strength of the radiative transition and by significantly increasing the non-radiative decay rate. We attribute both changes mainly to the distortion of the planarity of the perylene core. Bromine substituents reduce the fluorescence quantum yield by up to two orders of magnitude by opening an internal conversion channel.

1. Introduction

Perylenediimides (PDIs) are very stable, chemically inert materials possessing high fluorescence quantum yields (QYs), which causes their wide application in industry and scientific research. Nonsubstituted PDIs have very low solubility, so they are used as high quality industrial pigments, especially for automobiles [1,2]. Solubility enhancing substituents open new potential applications of PDIs. Due to advantageous properties, such as strong absorption in VIS region, high thermal and photo stability, low cost and good electron accepting properties PDI derivatives they were tested for application organic solar cells as sensitizers [3,4], as electron acceptors in non-fullerene organic solar cells [4–14], or as photosensitizers in dye-sensitized solar cells [15]. PDI compounds possess *n*-type conductivity, so they were also tested for application in organic field effect transistors [16–20]. High fluorescence yield, a broad fluorescence spectrum and high photostability make PDIs an excellent material for organic light emitting diodes [21–25] and for the development of organic solid-state lasers [26–28]. PDI compounds were used in luminescence solar concentrators [2,29,30]. Water-soluble PDI compounds were also applied as labels in fluorescence microscopy [31].

High fluorescence QY of PDIs, reaching 100% in solutions and about 90% in solid films, is one of the main attractive properties of these materials in the photonic applications [2,32,33]. However,

nonsubstituted PDIs have poor solubility and are prone to crystallization in solid state, therefore their substitution is essential for practical applications. Substituents used to modify PDI solubility and film formation properties also influence their spectroscopic properties and fluorescence QY [27,32–37]. The fluorescence QY typically drops down. In order to better control the fluorescence QY, it is essential to better understand the quenching mechanisms.

In this research we investigated spectroscopic properties of nine newly synthesized PDIs with various numbers of 4-tert-butylphenoxy (tBP) or bromine substituents. We analyse dependences of the fluorescence decay dynamics and its yield on the number and type of substituents. We demonstrate that substituents significantly influence both radiative and non-radiative decay rates causing a significant reduction of the fluorescence QY. Bromine substituents open an internal conversion channel. The internal conversion rate strongly increases with the number of attached Br atoms.

2. Experimental details

2.1. Material synthesis

Perylene-3,4,9,10-tetracarboxylic acid dianhydride PDA, solvents and reagents were obtained from commercial sources and were used as received. The synthesized materials were characterized by NMR. NMR

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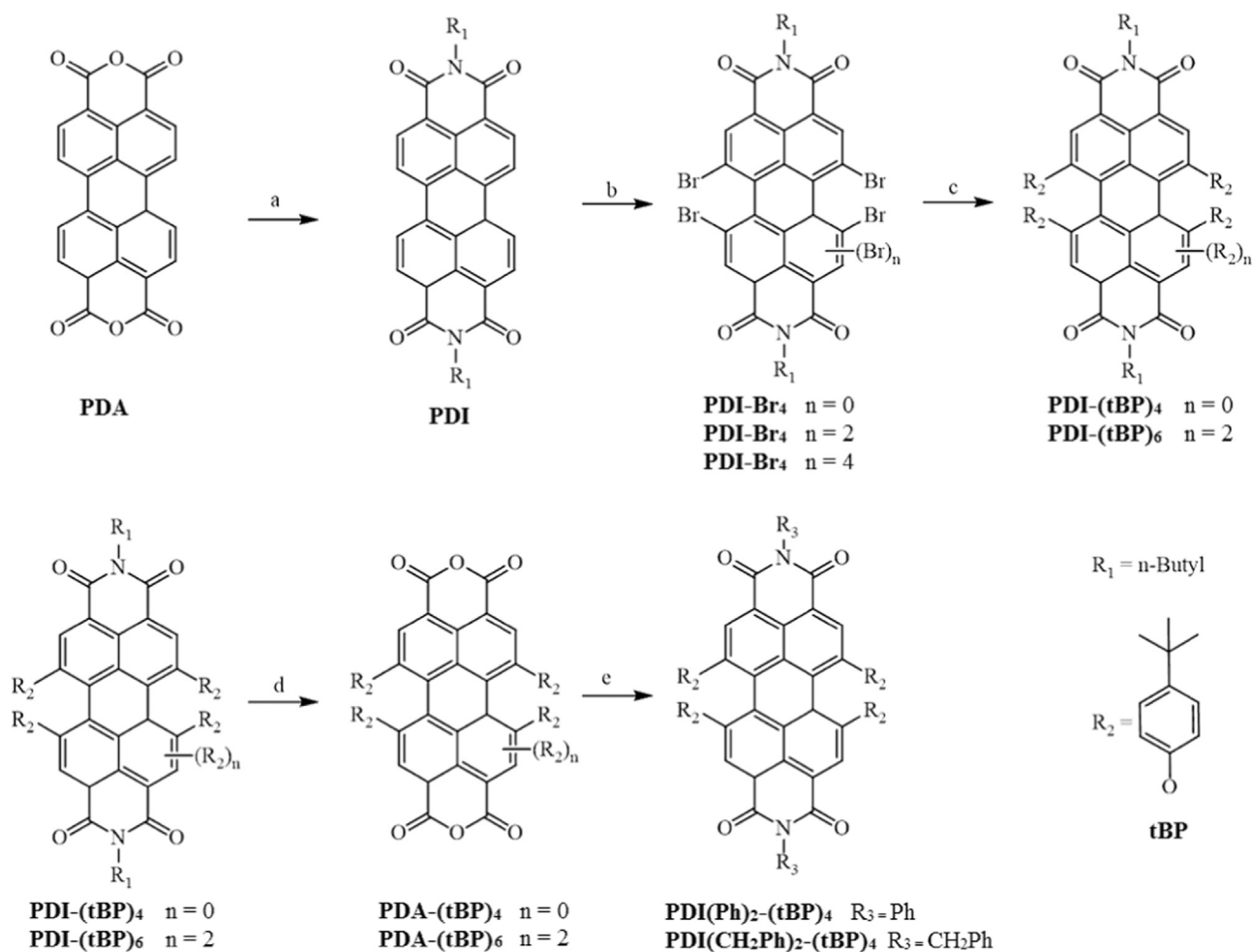


Fig. 1. Chemical structures of the investigated compounds and their synthesis routes: a) $n\text{BuNH}_2$, NMP, 150 °C. b) NBS, H_2SO_4 , 60 °C. c) KOH, 4-tBP, NMP, Ar, 80 °C. d) KOH, tert-BuOH / H_2O , Δ . e) PhNH_2 or PhCH_2NH_2 , NMP, 150 °C.

spectra were recorded on Bruker Ascend 400 (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) using residual solvent peaks as internal standards. Data for ^1H NMR are recorded as follows: a chemical shift (δ , ppm), multiplicity ($s = \text{singlet}$, $d = \text{doublet}$, $t = \text{triplet}$, $q = \text{quartet}$, $m = \text{multiplet}$ or unresolved, broad $s = \text{broad singlet}$, integration, coupling constant in Hz). Data for ^{13}C NMR are reported in terms of the chemical shift (δ , ppm). Silica gel 60 F254 aluminium plates (Merck) were used for TLC analysis. The synthesis routes are presented in Fig. 1.

2.1.1. Synthesis of PDI

PDA (392 mg, 1 mmol) and *n*-butylamine (2.93 g, 3.96 mL, 40 mmol) were added to *N*-methyl-2-pyrrolidone (NMP) (20 mL) under dynamic argon atmosphere. The reaction mixture was heated at 150 °C for 16 h. The reaction mixture was cooled to room temperature, poured on crushed ice (100 g) and stirred for 1 h. Precipitate was filtered, washed with water (3×20 mL) and methanol (3×20 mL), and dried in air at 60 °C to constant weight. Yield of **PDI** was 492 mg (98%).

2.1.2. Synthesis of PDI-Br₄, PDI-Br₆, and PDI-Br₈

PDI (502 mg, 1 mmol) was added to conc. H_2SO_4 (25 mL) and stirred at 60 °C until the starting material was fully dissolved (~ 1 h). *N*-Bromosuccinimide (NBS) was added (712 mg, 4 mmol for **PDI-Br₄**, 1068 mg, 6 mmol for **PDI-Br₆**, and 1780 mg, 10 mmol for **PDI-Br₈**) in portion-wise (4×178 mg for **PDI-Br₄**, 6×178 mg for **PDI-Br₆**, and 10×178 mg for **PDI-Br₈**) for 1 h, 1.5 h and 2 h, respectively, at 60 °C. The reaction mixture was stirred for additional 6–8 h at 60 °C. The reaction mixture was cooled to room temperature, poured on crushed ice (100 g)

and stirred for 1 h. Precipitate was filtered, washed with water (3×20 mL) and dried in air at 60 °C to constant weight. The crude product was purified by column chromatography on silica gel, eluting with toluene. Yield of the compounds was (90–95%).

PDI-Br₄. ^1H NMR: δ 8.85 (s , 4H), 4.27–4.21 (m , 4H), 1.76 (dt , $J = 15.2, 7.6$ Hz, 4H), 1.49 (dq , $J = 14.7, 7.4$ Hz, 4H), 1.02 (t , $J = 7.3$ Hz, 6H). ^{13}C NMR: δ 162.2, 136.1, 129.1, 128.2, 124.0, 122.4, 122.7, 40.7, 30.2, 20.3, 13.8.

PDI-Br₆. ^1H NMR: δ = 4.26–4.20 (m , 2H), 4.17–4.11 (m , 2H), 1.72–1.66 (m , 4H), 1.44–1.39 (m , 4H), 0.94 (t , $J = 7.5$, 6H). ^{13}C NMR: δ = 160.1, 133.5, 132.8, 132.1, 127.6, 125.8, 121.9, 42.3, 30.1, 20.4, 13.9.

2.1.3. Synthesis of PDI-(tBP)₄ and PDI-(tBP)₆

PDI-Br₄ (409 mg, 0.5 mmol) or **PDI-Br₆** (504 mg, 0.5 mmol), respectively, was added in portion to mixture of tBP (450 mg, 3 mmol for **PDI-(tBP)₄**, and 600 mg, 4 mmol for **PDI-(tBP)₆**) and potassium hydroxide (168 mg, 3 mmol for **PDI-(tBP)₄**, and 224 mg, 4 mmol for **PDI-(tBP)₆**) in NMP under dynamic argon atmosphere. The reaction mixture was stirred at 80 °C for 6 and 8 h, respectively. The reaction mixture was cooled to room temperature, poured on crushed ice (100 g) and stirred for 1 h. Precipitate was filtered, washed with water (3×20 mL) and dried in air at 60 °C to constant weight. The crude product was purified by column chromatography on silica gel, eluting with toluene and dichloromethane (DCM) mixture (19:1). Yield of **PDI-(tBP)₄** and **PDI-(tBP)₆** was 80% and 70%, respectively.

PDI-(tBP)₄. ^1H NMR: δ 8.25 (s , 4H), 7.28–7.23 (m , 8H), 6.88–6.83 (m , 8H), 4.18–4.11 (m , 4H), 1.68 (dt , $J = 15.1, 7.5$ Hz, 4H), 1.42

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