Novel derivatives of regioisomerically pure 1,7-disubstituted perylene diimide dyes bearing phenoxy and pyrrolidinyl substituents: Synthesis, photophysical, thermal, and structural properties

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Two new isomerically pure 1,7-substituted perylene-bisimide derivatives namely; 1,7-Di(4-tert-butylphenoxy)-N,N′-bis[2-(diethylamino)ethyl]-3,4,9,10-perylene-tetracarboxylic diimide (6) and 1,7-Di(pyrrolidinyl)-N,N′-bis [2-(diethylamino)ethyl]-3,4,9,10-perylene- tetracarboxylic diimide (7), have been synthesized and their electronic absorption, steady-state fluorescence, and thermal properties were studied. Both compounds show good solubility in a range of organic solvents. Attachment of two electron donating tert-butyl-phenoxy groups at the 1,7-positions in (6) resulted in a red shifted absorption band with absorption maximum at 543 nm. UV–visible absorption spectrum of (7) shows a broad absorption band within the red region. Absorption maximum of lowest energy transition now shifts to 704 nm. Both compounds (6) and (7) exhibit low fluorescence quantum yields of 0.133 and 0.007, respectively. Density functional theory (DFT) calculations revealed that the attachment of electron donating groups at 1,7-positions of PDIs, results in an increase in frontier orbitals energy levels. Observed energy increase in HOMO is larger in each case, compared to the energy increase in LUMO levels. Calculated band gaps for (6) and (7) are 2.462 and 2.128 eV respectively.

1. Introduction

Perylene-3,4,9,10-tetracarboxylic acid diimide derivatives, popularly called the perylene diimides (PDIs) represents an outstanding class of organic compounds that has been utilized in a diverse applications such as field effect transistors [1], logic gates [2], organic solar cells [3], sensors [4], organic light-emitting diodes [5], photosensitizers [6] optical switches [7], and more. Molecular structure of PDIs involve a rigid aromatic core (perylene) which is substituted with dicarboxylic acid imide groups at the peri-positions. The extension of π-conjugation between the electron-rich perylene core and strongly electron-withdrawing imide groups, results a red shifted electronic absorption band that is observed at ~ 520 nm with, characteristic progressions that are vibronic in origin [8]. Consequently compounds in this class display high chemical, thermal, electrochemical and photochemical stability as well as high fluorescence quantum yields approaching to unity. Accordingly, number of excellent reviews have been published, focusing on, synthesis and structure-property relationships of various PDI structures [9,10], applications of PDIs in photonics [1,11,12], organic electronics [13–16], and about their supramolecular structures [17] involving hydrogen-bonding interactions [18] and organometallic structures [19].

The two major strategies applied to modify structure of PDIs involve different N-substitutions at the "peri" (imide) positions and substitution at the "bay" region (1-, 6-, 7-, and 12-positions). Substitution at the imide positions can be used to tune aggregation and solubility properties of the corresponding imides [20] but have little effect on the electronic and optical properties such as absorption, fluorescence, and HOMO/LUMO energies due to the frontier molecular orbital nodes that are available on the imide nitrogen atoms. Having planar rigid aromatic core, such structures exhibit strong π-π molecular interactions. Substitution at the bay position normally consist of two or four substituents, with a prior halogenation of perylene-3,4,9,10-tetracarboxylic bisanhydride (PBA) to yield 1,7-dibromoperylene-3,4,9,10-tetracarboxylic bisanhydride [21] or 1,6,7,12-tetrachloro perylene-3,4,9,10-tetracarboxylic bisanhydride [22,23]. Bay position functionalization provides a tool for controlling the opto-electronic properties of PDIs, as well as significantly increasing the solubility of the dyes by inducing a twist in the perylene core [24–26]. Notably, bromination of PBA mainly leads to regioisomeric mixture of 1, 6- and 1,7-

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dibromoperylene-3,4,9,10-tetracarboxylic bisanhydride [27]. Recent studies have demonstrated that the electrochemical and optical properties of 1,7- and 1,6-substituted perylene bisimides can be distinctly different [28–31]. Recently a route for the synthesis of the isomerically pure 1,7-dibrominated perylene compounds have been reported [32]. Reported synthons involve 1,7-dibromoperylene-3,4,9,10-tetracarboxylic tetrabutylester as a key compound that can be utilized en route to the 1,7-dibromoperylene-3,4,9,10-tetracarboxylic dibutylester monoanhydride, and 1,7-dibromoperylene-3,4,9,10-tetracarboxylic bisanhydride, that are excellent starting materials for the synthesis of a large variety of bay-area-substituted compounds.

As a consequence, synthesis of new and isomerically pure bay substituted PDIs and investigation of their structural, optical, photophysical, and thermal properties are of still great interest. In this context, herein we present the synthesis and characterization of two novel symmetrically substituted PDI derivatives bearing 2-(diethylamino) ethylamine groups at imide positions and phenoxy or pyrrolidinyl groups attached at 1,7-bay positions, and discuss their structural, optical, photophysical, and thermal features.

2. Experimental

2.1. Materials

The commercially available chemicals and solvents employed in the study were purchased from either Merck Millipore or Sigma-Aldrich. Chemicals and reagents were used as received, without further purification unless otherwise stated. Solvents used for chromatographic separations were purified according to standard purification methods [33]. Moisture/air-sensitive reactions were performed under inert nitrogen (N_2) atmosphere. Thin layer chromatography (TLC) was performed on aluminium TLC plates, silica gel coated with fluorescent indicator F254. Chromatographic purification was done on silica gel pore size 60 Å, 70–230 mesh, 63–200 μm.

2.2. Equipment

Melting points were determined with Mel-Temp® capillary melting point apparatus and were uncorrected. Nuclear magnetic resonance (NMR) spectra were measured and recorded on a Bruker Avance 400 MHz NMR spectrometer. FTIR spectra were recorded with a Varian-660 IR spectrometer in the 4000–400 cm^{-1} spectral range in the transmittance mode. Reported measurements were recorded using KBr pellets of the sample. UV–visible measurements were recorded on a PG-Instruments T80+ spectrophotometer. Fluorescence emission spectrums were recorded on a Shimadzu RF-5301PC Spectrofluorophotometer. Spectral data were processed into graphs with Spectragryph optical spectroscopy software [34], and Origin (OriginLab, Northampton, MA). All solvents employed for spectral measurements were of spectroscopic grade. High resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G1 mass spectrometer, using ESI-TOF (electrospray ionization-time of flight). Thermogravimetric analysis (TGA) curves were recorded on a Setaram Labsys TG-DTA system, under N_2, with a heating rate of 10 °C min^{-1} (for compound (6)) and PerkinElmer Pyris 1 thermogravimetric analyser, under N_2, with a heating rate of 10 °C min^{-1} (for compound (7)).

2.3. Solubility

Solubilities are determined at a concentration of 10 mg ml^{-1} in solvents at 25 °C (RT) and 60 °C (Hot). (+): soluble; (+ −): partially soluble (3–7 mg ml^{-1}); (−): insoluble.

2.4. Photophysical parameters

2.4.1. Fluorescence quantum yields

Fluorescence quantum yields (Φ_F) were determined by comparative method [35]. Φ_F of the test samples were calculated using Eq. (1):

$$\Phi_u = \Phi_{st} \left(\frac{Grad_u}{Grad_{st}} \right) \left(\frac{\eta_u^2}{\eta_{st}^2} \right) \tag{1}$$

where Φ_u is the fluorescence quantum yield of the unknown sample, Φ_{st} is the fluorescence quantum yield of the standard sample, $Grad_u$ is the gradient from the plot of integrated fluorescence intensity versus absorbance of the unknown, $Grad_{st}$ is the gradient from the plot of integrated fluorescence intensity versus absorbance of the standard sample, η_u is the refractive index of the solvent for the unknown sample and, η_{st} is the refractive index of the solvent for the standard sample. Low concentrations were maintained in order to rule out reabsorption effects.

2.5. Thermal analysis

Thermogravimetric analyses were done under an inert N_2 atmosphere, with a heating rate of 10 °C min^{-1}.

2.6. Quantum chemistry computations

Theoretical calculations were performed at density functional level (DFT). Hybrid B3LYP (Becke-Lee-Young-Parr) functional [36–39] and Ahlrichs def2-SVP basis set [40,41] for geometry optimization (ground state) and property calculations were employed. Vibrational frequency and time dependent density functional (TD-DFT) calculations were also performed by using same functional and basis set, at gas phase. Grimme's DFT-D3(BJ) [42,43] dispersion correction method were also used. All quantum chemical calculations were performed by using ORCA [44] version 3.0.3 software. ORCA version 3.0.3 imposes Tamm-Dancoff approximation [45,46] (TDA) for excited state calculations when hybrid functionals are employed, therefore all TD-DFT calculations presented here utilizes TDA. Frequency calculations produced no imaginary frequencies, suggesting the optimized geometries to be of true minimum energy structures. TightSCF criteria were employed as implemented in ORCA v3.0.3.

2.7. Synthesis

2.7.1. Synthesis of perylene-tetracarboxylic tetrabutyl ester (2)

A mixture of PDA (1) (0.980 g, 1 equivalent), 1,8-Diazabicyclo [5.4.0]undec-7-ene (DBU) (4 equivalent), n-butanol (1.50 g, 8 equivalent) in 12 ml of N,N-Dimethylformamide (DMF) was stirred at 60 °C for 0.5 h. 1-bromobutane (2.74 g, 8 equivalent) was added to the mixture and a subsequent addition of another 9 ml of DMF, and further stirred for 3 h. After cooling to room temperature, the resulting mixture was poured into water (100 ml) and stirred for 15 min, after which it was filtered. The crude residue after the filtration process was subjected to column chromatography on silica gel, eluting with dichloromethane (CH_2Cl_2), to give titled compound (2) as a golden-orange solid (yield, 1.54 g). IR (KBr): 3247, 2964, 2330, 1730, 1587, 1447, 1304, 1034, 810, 737, 606 cm^{-1}; $\lambda_{max\,CHCl_3} = 472$ nm (ε = 30,000) and 443 nm (ε = 23,900,); $\lambda_{max\,DMF} = 469$ nm (ε = 46,100), and 441 nm (ε = 38,700); and, ^1H NMR (400 MHz, CDCl$_3$): 1.04 (t, 12H), 1.55 (m, 8H), 1.83 (m, 8H), 4.37 (t, 8H), 7.80 (d, 4H), 7.85 (d, 4H); ^{13}C NMR (100 MHz, CDCl$_3$): 13.8, 19.3, 30.7, 65.3, 121.1, 128.3, 128.5, 130.1, 132.4, 168.5. HRMS (ESI-TOF): calcd. for $C_{40}H_{46}O_8$ [M + 2H]$^+$: 654.3193, found: 654.3136.