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Spectroscopic properties of diketopyrrolopyrrole derivatives with long alkyl chains

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ABSTRACT

The diketopyrrolopyrrole derivatives with long alkyl chains were synthesised and spectrally characterised. Experimental spectroscopic techniques were supplemented by the DFT calculations of equilibrium geometries, normal mode frequencies and time-dependent DFT simulated UV–vis spectra. Comparison between the symmetrical and unsymmetrical substitution of alkyl chains resulted in some changes like bathochromic shift of absorption, excitation and emission spectra, significant reduction of molar absorption coefficient in UV–vis range, increase of fluorescence quantum yield, and slight increase of fluorescence lifetimes. The influence of the length of the alkyl chain on the properties of material was also discussed. The experimental spectroscopic data together with the calculated results show that presence of the alkyl substituent at the nitrogen atom influences more on the properties of the investigated DPPs than the length of attached chain.

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1. Introduction

The diketopyrrolopyrroles (DPPs) are organic pigments which attract attention of the scientific community in recent years. This focus on the DPP derivatives is not caused only by their direct application as dyes or pigments (paints, printing etc.) but rather by the possibility of use them in various other ways. The other reasons for this interest is relatively simple synthesis of the DPPs, possibility of the chemical modifications for tuning the physical properties, and stability [1]. There are numerous reports on the use of DPP derivatives as organic field-effect transistors [2–5], organic solar cells [5–12], organic light emitting diodes [13,14] or fluorescent sensors [15].

From the technological point of view it is important to have as much information about the material as it is possible. Attachment of various substituents including alkyl chains influence the properties of the material such as solubility in solvents or ability to self organisation. On the other hand, this substitution can influence on the spectral properties of material. In the case of the application in generally speaking organic photovoltaics the considered material should be spectroscopically characterized in details. This is the main purpose of this work – to provide a detailed spectroscopic

data about three new DPP derivatives focusing on the properties important in photovoltaic applications.

2. Experimental

2.1. Synthesis

Materials. 3,6-Di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP) [16] was synthesized according to the literature. All other reagents and solvents were purchased from commercial sources. All reaction containers were flame dried under vacuum before use.

2-(2-decyltetradecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP1) A solution of 2-decyltetradecylbromide (13.9 g, 33.3 mmol) in dried *N,N*-dimethylformamide (DMF) (10 mL) was added dropwise to a mixture of DPP (10 g, 33.3 mmol) and K₂CO₃ (4.6 g, 33.3 mmol) in DMF (250 mL) at room temperature. The mixture was heated up to 80 °C for 4 h under a nitrogen atmosphere. The solution was cooled to room temperature, poured into 500 mL of ice water, and then extracted by using dichloromethane. After drying in vacuum, the crude product was purified by silica gel chromatography using dichloromethane as eluent to obtain a dark orange solid powder (4.5 g, yield 21%). ¹H NMR (CDCl₃, 300 MHz): 9.09 (s, 1H), 8.45 (d, 1H), 8.05 (d, 1H), 7.70 (d, 1H), 7.55 (d, 1H), 7.25 (m, 2H), 4.56 (d, 2H), 1.81 (m, 1H), 1.6–1.0 (m, 39H), 0.85 (m, 6H).

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2,5-bis(2-octylododecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP2) It was synthesized with a similar procedure as described for the **DPP1** to afford **DPP2** (Yield: 90%) by using 2 equivalent fraction of 2-octylododecylbromide reacted with one equivalent of **DPP**. ¹H NMR (CDCl₃, 300 MHz): 8.65 (d, 2H), 7.66 (t, 2H), 7.23 (d, 2H), 4.54 (d, 2H), 1.85 (m, 1H), 1.7–1.0 (m, 64H), 0.80–0.89 (m, 12H).

2,5-bis(2-decyltetradecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP3) It was synthesized with a similar procedure as described for the **DPP2** to afford **DPP3** (Yield: 85%) by using 2-decyltetradecylbromide instead of 2-octylododecylbromide. ¹H NMR (CDCl₃, 300 MHz): 8.62 (d, 2H), 7.64 (t, 2H), 7.24 (d, 2H), 4.55 (d, 2H), 1.83 (m, 1H), 1.6–1.0 (m, 80H), 0.80–0.88 (m, 12H).

2.2. Spectroscopy

The infrared absorption spectra of the investigated DPPs were recorded at room temperature in the middle infrared range with FT-IR Bruker Equinox 55 spectrophotometer. The samples were prepared by grinding the crystals in agate mortar and mixing them with spectroscopic grade potassium bromide (KBr). The pellets were made from the powder using a simple press and a pure KBr pellet was used as a reference.

The room temperature Raman spectra of the DPPs were collected with a Horiba Jobin Yvon LabRam HR800 spectrometer using excitations at $\lambda_{\text{ex}}=488$ and 514 nm (Stabilite 2017 Ar ion laser) and $\lambda_{\text{ex}}=633$ nm (He-Ne laser) for DPP1. The last two excitation lines gave the spectra of rather poor quality and for samples DPP2–DPP3 only the excitation 488 nm allow us to record the spectrum. The power of the laser beam at the sample was less than 13 μW to avoid damages of the sample.

The ground state absorption spectra were recorded with an UV–vis Varian Cary 4000 spectrophotometer in a 10 mm path length quartz cuvette over the range of 200–900 nm. The steady state fluorescence emission and excitation spectra were recorded with a Hitachi F-4500 fluorimeter at varied excitation and observation wavelengths in the range of 285–800 nm. Fluorescence decay curves were recorded with PTI EasyLife fluorimeter with an emission cutoff filter at 490 nm using pulsed LED excitation source at 280 nm. Titanium dioxide nanopowder dispersed in isopropanol was used to record the instrumental response function (IRF). Fluorescence lifetimes were estimated by fitting the decay curves using a deconvolution procedure implemented into Fluorescence Decay Analysis Software 1.3, FluorTools.

The fluorescence quantum yields (Φ_F) were determined using the formula [17]

$$\Phi_F = \Phi_{FSt} \cdot \frac{F_x}{F_{St}} \cdot \frac{1 - 10^{-A_{St}(\lambda_{\text{ex}})}}{1 - 10^{-A_x(\lambda_{\text{ex}})}} \cdot \frac{n_x^2(\lambda_{\text{em}})}{n_{St}^2(\lambda_{\text{em}})} \quad (1)$$

where A is the absorbance, F is the area under the fluorescence curve, n is the refraction index, λ_{ex} and λ_{em} are excitation and emission wavelength, respectively. The subscripts x and St refer to the sample and to the fluorescence standard, respectively. As a fluorescence standard Rhodamine 6G dissolved in ethanol was used ($\Phi_{FSt}=0.94$) [18].

Radiative (k_R) and nonradiative (k_{NR}) decay rates were calculated according the formulas [19,20]

$$k_R = \frac{\Phi_F}{\tau} \quad (2)$$

$$k_{NR} = \frac{1}{\tau} - k_R \quad (3)$$

where τ is fluorescence lifetime.

Transition dipoles values, μ_{01} , for $S_0 \rightarrow S_1$ (ground and first excited electronic states, respectively) electronic transition were calculated based on the experimental absorption spectra as

$$\mu_{01} = 0.096 \cdot \sqrt{\frac{\int \epsilon(\nu) d\nu}{\nu^{\text{MAX}}}} \quad (4)$$

where μ_{01} is in D, molar absorption coefficient $\epsilon(\nu)$ is in $\text{M}^{-1} \text{cm}^{-1}$, and ν is in cm^{-1} (ν^{MAX} is wavenumber corresponding to the absorption band maximum) [21].

Electronic spectroscopy measurements were done for dyes dissolved in spectroscopic grade chloroform purchased from Sigma-Aldrich. The fluorescence quantum yields were calculated based on results recorded for the samples of varied low concentration in order to minimize a reabsorption effect (maximum absorbance less than 0.1). Presented UV–vis absorption and fluorescence spectra as well as fluorescence decay curves were recorded for dyes solutions of 1×10^{-5} M concentration. All measurements were done at room temperature.

2.3. Quantum chemical calculations

The quantum chemical calculations of the molecules DPP1, DPP2, and DPP3 were performed using the Gaussian 03 program package [22]. The calculations were carried out for isolated molecules using the density functional theory (DFT) with Becke's three parameter exchange functional combined with the Lee–Yang–Parr correlation functional (B3LYP). The initial geometries were build using GaussView program. The standard 6-31G(d) basis set was used for geometry optimizations and calculations of the normal modes frequencies. To improve the interpretation of the experimental UV–vis spectra we performed also the calculations of the transition energies via time-dependent density functional theory (TD-DFT). Time dependent DFT calculations (B3LYP/6-31G(d)) were performed using the equilibrium geometries of the molecules obtained in the previous step. The first 50 optical transitions were calculated. To convolute the transition energies and oscillator strengths into the absorption spectra, the GaussSum program was used [23]. The spectra were generated assuming FWHM (Full Width at Half Maximum) parameters at 3000 cm^{-1} for all transitions. Additionally the influence of solvent (chloroform) was taken into account using the Polarized Continuum Model (PCM) as implemented in the Gaussian 03 software.

3. Results and discussion

The structure and synthesis of DPP molecules containing alkyl chains are shown in Fig. 1. The DPP1 was synthesized in one-step reaction of DPP with one equivalent molar ratio of 2-decyltetradecylbromide under K_2CO_3 as a base in DMF at 80 °C. DPP2 and DPP3 were prepared by similar reaction through adding two equivalent molar ratio of alkylbromides. All compounds can be purified by column chromatography to afford DPP1, DPP2, and DPP3.

The equilibrium geometries of the investigated molecules are presented in Fig. 2. One can notice that the DPP core is flat in all investigated molecules, one thiophene ring is almost in-plane with the DPP core while the other thiophene ring is twisted with regard to the DPP core. Twisting of only one thiophene ring in similar DPP derivative has been also reported by Naik and coworkers [24]. Such situation causes that thiophene rings will not be equivalent and their normal mode vibrations can be separated. The main difference between the DPPs is of course the NH group instead of alkyl chain in DPP1. DPP2 and DPP3 differs mainly in alkyl chain length.

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