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Photophysical characterization of 2,9-bis(7-benzothiazole-9,9′-didecylfluoren-2-yl)perylene diimide: a new standard for steady-state fluorescence anisotropy

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Abstract

The absorption, fluorescence excitation and emission spectra have been obtained in solution for 2,9-bis(7-benzothiazole-9,9-didecylfluoren-2-yl)perylene diimide. Efficient resonance energy transfer from the fluorenyl group to the perylene ring center was observed. Interestingly, fluorescence emission was detected from the second excited electronic state of the perylene ring system. Fluorescence excitation anisotropy spectra obtained at room temperature exhibited a parallel orientation of the main absorption and emission band transition moments for the perylene-based dye in CH_2Cl_2. The value of excitation fluorescence anisotropy for the perylene dye in solution approached the theoretical maximum limit ($r \approx 0.4$), and indicated that the rotational correlation time exceeded the lifetime of the first excited state. These results provide the basis for using this unique compound as an anisotropy reference standard.

Keywords: Perylene-based dyes; Absorption; Fluorescence; Excitation anisotropy; Energy transfer

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1. Introduction

Anisotropy measurements provide important information about the electronic structure of probe molecules. For example, in biological systems this information can yield insight into cellular membrane potential and transport properties, as well as various physiological environments [1,2]. The burgeoning growth of polymeric guest/host composites in fields such as liquid crystal displays, electro-optic polymer modulators, and polymer light-emitting diodes places increased demand on the ability to accurately characterize the polarization or anisotropy of the materials. However, relatively few organic probes exhibit a high enough value of anisotropy (in solution at room temperature) to be useful as a standard for anisotropy measurements. Thus, the development of such probes is of paramount importance and necessitates both synthetic and photophysical characterization efforts.

Perylene-based organic compounds are of broad interest owing to their wide range of potential applications including electron-transporting components in organic light-emitting diodes [3], semiconducting materials for electrophotography [4], photovoltaic materials for solar energy conversion [5], photorefractive materials for optical signal processing [6] and others. Derivatization of perylene with highly fluorescent fluorene derivatives [7] leads to considerable extension of the variety of their photophysical and photochemical properties. Therefore, the spectroscopic investigation of such compounds are of considerable interest. In this work we present the spectral studies of 2,9-bis(7-benzothiazol-9,9-didecylfluoren-2-yl)perylene diimide (**1**) with particular emphasis on excitation anisotropy and energy transfer.

Perylene diimide molecules, relative to the parent perylene [8,9], exhibit a red shift of the absorption maximum to a longer wavelength region ($\lambda_{max} = 510$–$530\,nm$) with an increase in the extinction coefficients up to $(50–100) \times 10^3\,M^{-1}\,cm^{-1}$ [4]. The position of λ_{max} is not very sensitive to the structure of N-substituents and a small spectral shift with different substituents suggests the π, π^* transitions of perylene diimide are localized in the perylene ring [4]. Compound **1** combines the perylene ring system with a fluorene derivative. This combination is expected to expand the variety of photophysical and photochemical properties of perylene-based organic dyes. The relatively elongated molecular geometry of **1** suggests it may exhibit

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a high value of the fluorescence anisotropy. Compound **1** in THF exhibited intramolecular energy transfer from the fluorenyl moiety to the perylene ring system upon UV excitation [7], which is important for development of new photoconductive materials. Therefore, the spectral behavior of **1** under different excitation conditions was central to our investigation.

2. Experimental

The symmetrically substituted 2,9-bis(7-benzothiazol-9,9-didecylfluoren –2-yl) (**1**) perylene diimide was synthesized as previously described [7]. All photophysical measurements were performed in CH_2Cl_2 at room temperature. Absorption spectra were recorded with a UV–VIS Cary-3 spectrophotometer. Steady-state fluorescence excitation anisotropy, excitation and emission spectra were recorded for the liquid solutions of **1** (2×10^{-6} M) in 10 mm path length cuvettes with a PTI Quantamaster spectrofluorimeter. The excitation anisotropy spectra were performed using three polarizers in T-format method [9] and polarized scattering signals were measured in different orientations for the pure solvent. Fluorescence quantum yield was measured by a standard method [9] relative to Rhodamine 6G in ethanol at room temperature [10].

3. Results and discussion

The molecular structure and absorption spectrum of compound **1** are shown in Fig. 1. The chemical structure of **1** consists of two chromophore systems: a perylene diimide core and fluorenyl terminal groups. The spectral properties of perylene diimide are not very sensitive to the structure of terminal groups. In contrast, the combination of the fluorenyl group with perylene diimide results in a blue shift of the position of λ_{max} of the fluorenyl moiety, owing to the electron-withdrawing nature of the diimide [7]. Perylene-based dye **1** in CH_2Cl_2 exhibited two strong absorption bands in the UV–VIS region. One band belonged to the perylene ring system with absorption maxima 460, 490, 526 nm and maximum extinction coefficient of $130 \times 10^3\ M^{-1}\ cm^{-1}$. The second exhibited absorption band (280–380 nm), with $\lambda_{max} = 345$ nm, was more complicated and consisted of the fluorenyl group absorption band and higher excited state absorption bands of the perylene diimide system.

The entire emission spectrum of **1** in CH_2Cl_2 is shown in Fig. 2. As can be seen, under excitation in the spectral region $\lambda_{exc} \geq 400$ nm, mainly one fluorescence band ($\lambda_{max} = 533$ nm) corresponding to the perylene diimide core was observed. Upon excitation in the shorter wavelength absorption band (345 nm), compound **1** exhibited two fluorescence contours. The low intensity fluorescence in the

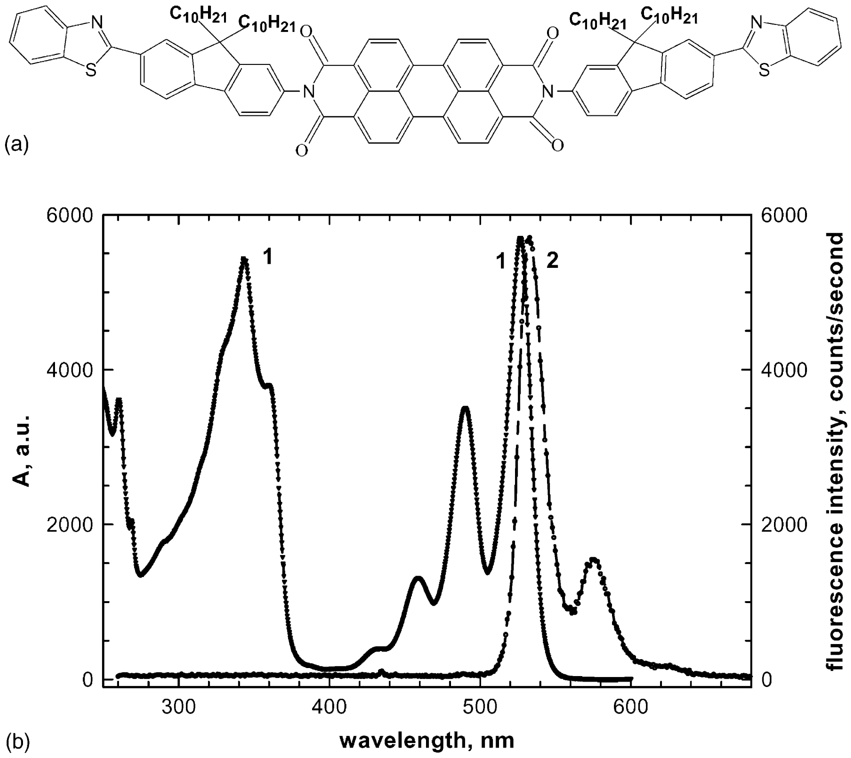

Fig. 1. (a) Chemical structure of perylene diimide dye **1** and (b) normalized UV–VIS absorption spectrum (1) and fluorescence emission spectrum with $\lambda_{exc} = 490$ nm (2) of **1** in CH_2Cl_2.

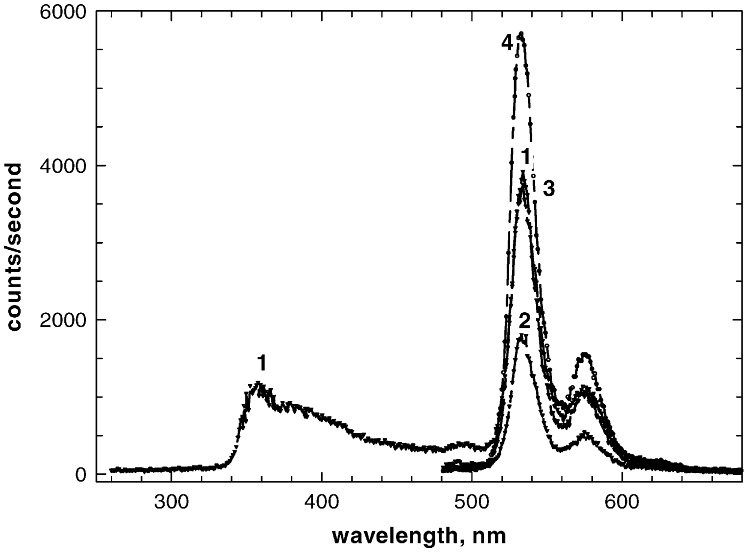

Fig. 2. Fluorescence spectra of compound **1** in CH_2Cl_2: (1) $\lambda_{exc} = 345$ nm; (2) $\lambda_{exc} = 460$ nm; (3) $\lambda_{exc} = 490$ nm; (4) $\lambda_{exc} = 525$ nm (excitation scattering lines removed).

spectral region 350 nm $\leq \lambda \leq$ 500 nm, can be attributed to the fluorenyl groups, partially overlapping with the perylene diimide main absorption band. Our measurements show that many fluorenyl compounds themselves are characterized by a high fluorescence quantum yield [11]. Decrease of the fluorenyl fluorescence intensity in perylene-based dye **1** suggested efficient intramolecular resonance energy transfer [9] from the fluorenyl group to the perylene ring system.

Fig. 3 shows the excitation spectra of **1** in CH_2Cl_2 with observation (λ_{obs}) at 535 nm. There is a good correlation between absorption and excitation spectra (Figs. 1 and 3). In order to discern whether the observed fluorescence emission was due to direct energy transfer from the fluorenyl to perylene moiety, or due to trivial radiative energy transfer via absorption of the fluorene emission by the perylene group, excitation spectra were recorded as a function of dye concentration. The intensity of the spectra (over the entire spectral range) changed linearly in proportion to solution concentration, demonstrating the direct resonance energy transfer mechanism was operative. For the case of trivial radiative energy transfer such a proportional change of the excitation spectra would not be expected, since the degree of the re-absorption (of the fluorene emission) by the perylene group also depends on the dye concentration.

Under short wavelength excitation (λ_{exc} = 280–295 nm) two weak fluorescence contours (λ_{max} = 350 nm and

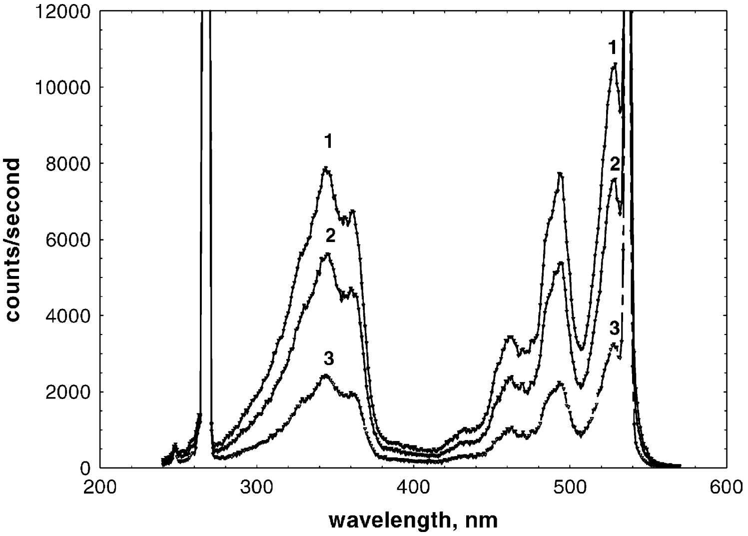

Fig. 3. Excitation spectra of compound **1** in methylene chloride ($\lambda_{obs} = 535$ nm) under the different concentrations: (1) 1.4×10^{-6} M; (2) 8.9×10^{-7} M; (3) 3.3×10^{-7} M, (sharp line) at 265 nm corresponds to the second-order scattering light.

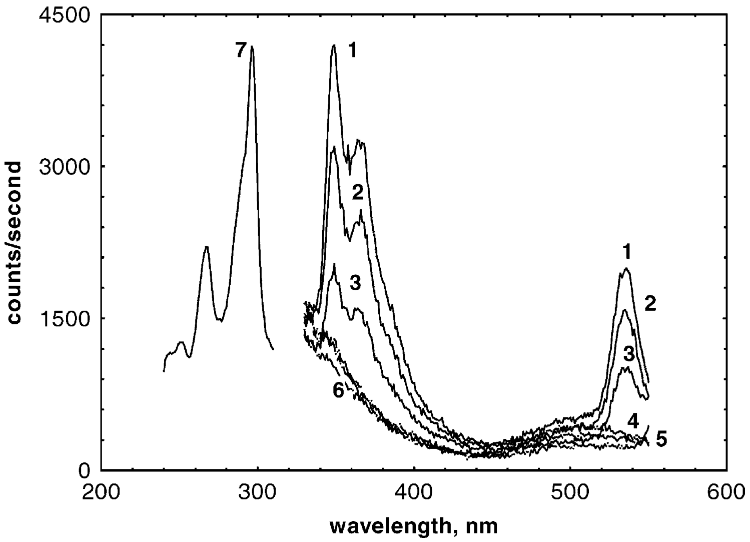

Fig. 4. Fluorescence (1–6) and excitation (7) spectra of compound **1** in CH_2Cl_2: (1) $\lambda_{exc} = 295$ nm; (2) $\lambda_{exc} = 290$ nm; (3) $\lambda_{exc} = 282$ nm; (4–6) corresponding scattering light; (7) $\lambda_{obs} = 350$ nm.

533 nm) were observed, as presented in Fig. 4. The excitation spectrum of the short wavelength fluorescence band, $\lambda_{obs} = 350$ nm (Fig. 4, curve 7), corresponded to a higher electronic excited state absorption (higher than S_1) of the perylene core. To demonstrate that this behavior was, in fact due to emission from a higher excited state, the emission spectra were measured upon excitation at three different wavelengths corresponding to the major absorption peaks that were attributable to the higher excited state (282–295 nm), e.g. S_2. As illustrated in Fig. 4, the emission intensity (both $\lambda_{max} = 350$ nm and $\lambda_{max} = 533$ nm) was directly proportional to the intensity of the corresponding absorption maxima (282–295 nm). Therefore, the emission band with $\lambda_{max} = 350$ nm is related to fluorescence from a higher excited electronic state. This is in accord with the observation of the fluorescence from higher excited electronic states for 1,12-benzoperylene [12], azulene, pyrene and its derivatives [13], 1,2-benzanthracene and fluorantrene [14], rhodamine [15], and polymethine dyes [16].

The excitation anisotropy spectrum for **1** in CH_2Cl_2 is presented in Fig. 5. The main features were the existence of three different electronic transitions. The spectral region with $\lambda_{exc} > 430$ nm corresponded to the main absorption band of perylene diimide; $\lambda_{exc} \approx 380$ nm corresponded to the second absorption band of perylene, resulting from the transverse absorption of the perylene ring system (with the direction of the dipole moment approximately perpendicular to the long molecular axis [9]).The maximum extinction

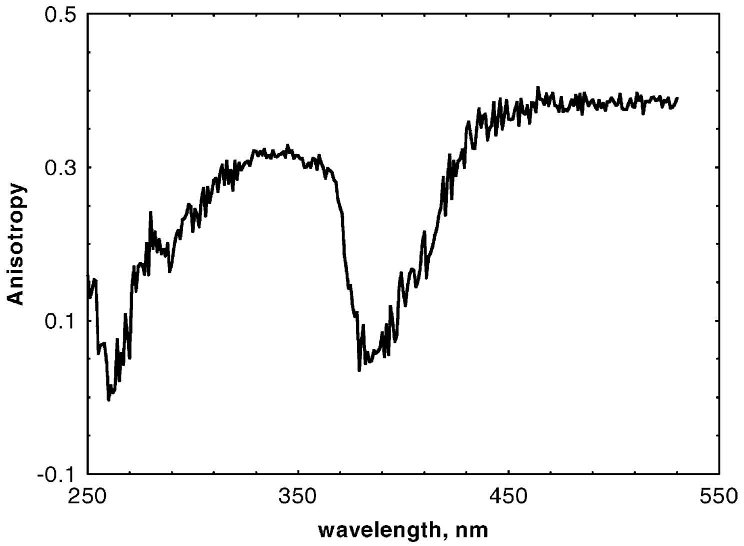

Fig. 5. Excitation anisotropy spectrum for compound **1** in CH_2Cl_2 at room temperature ($\lambda_{obs} = 540$ nm).

coefficient of this band was less than $1500\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ [9], a probable reason why this band was not observed in the absorption spectrum (Fig. 1b). The spectral range with $\lambda_{\mathrm{exc}} = 320$–$360\,\mathrm{nm}$ corresponded to the electronic transition of the fluorenyl group. More precise determination of the nature of the higher excited electronic states in the short wavelength UV region requires more detailed investigation and is beyond the scope of this work.

As shown in Fig. 5, excitation anisotropy of **1** in CH_2Cl_2 reached the value of $r \approx 0.38$–0.4 in the spectral region $\lambda_{\mathrm{exc}} > 450\,\mathrm{nm}$, approaching the calculated theoretical maximum of 0.4. This indicated a parallel orientation of the main absorption and emission band transition moments of the perylene ring system. A high value of anisotropy for **1** in CH_2Cl_2 at room temperature was determined by the short lifetime of the first excited electronic state, τ in comparison with the rotational diffusion correlation time, θ which is expressed as [9]

$$\theta = \frac{\eta V}{RT}$$

where η is the viscosity of the solution, T temperature in Kelvin, R the gas constant and V the volume of the molecule. Indeed, the calculation of θ for compound **1** in methylene chloride at room temperature gives $\theta \approx 150$–$200\,\mathrm{ps}$. The radiation lifetime $\tau_{\mathrm{R}} \approx 2.5\,\mathrm{ns}$ for the perylene ring system was calculated by the Birks and Dyson equation: [13]

$$\frac{1}{\tau_{\mathrm{R}}} = 2880\left(\frac{g_1}{g_2}\right)\left(\frac{n_{\mathrm{f}}^3}{n_{\mathrm{a}}}\right)\int\frac{\varepsilon(\nu)}{\nu}\mathrm{d}\nu \times \int F(\nu)\mathrm{d}\nu\left[\int\frac{F(\nu)}{\nu^3}\mathrm{d}\nu\right]^{-1} \quad (\tau_{\mathrm{R}}\ \text{in seconds})$$

in which g_1 and g_2 are the multiplicities of the ground and excited states (for singlet states $g_1/g_2 = 1$), n_{f} and n_{a} the mean refractive indices of the solvent over the wavelength range of the fluorescence and absorption bands ($n_{\mathrm{f}} \approx n_{\mathrm{a}} \approx 1.42$ for methylene chloride), $\varepsilon(\nu)$ the curve of molecular excitation coefficient plotted against wavenumber in $\mu\mathrm{m}^{-1}$, $F(\nu)$ the quantum intensity of fluorescence at wavenumber ν in $\mu\mathrm{m}^{-1}$. The lifetime of the first excited state can be obtained from the equation:

$$\tau = \tau_{\mathrm{R}}\Phi \approx 7.5\,\mathrm{ps}$$

where $\Phi \approx 0.003$ is the quantum yield of **1** in methylene chloride. These results show that $\tau \ll \theta$, corresponding to a high experimental anisotropy value.

4. Conclusions

We have presented an overview of the rather unusual spectroscopic properties of 2,9-bis(7-benzothiazol-9,9-didecylfluoren-2-yl)perylene diimide in methylene chloride. This compound was found to exhibit fluorescence emission from a higher excited electronic state at room temperature, previously, only observed for relatively few organic compounds [12–16]. Seemingly efficient direct energy transfer from the fluorenyl group to the perylene diimide core was demonstrated. The high value of fluorescence anisotropy of **1** in liquid solution indicated parallel orientation of the absorption and emission transition moments for the perylene ring system and short lifetime of the first excited state in comparison with its rotational correlation time. Due to its unique spectral properties, perylene diimide **1** can be used as a fluorescence standard of steady-state anisotropy in liquid solution at room temperature.

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