

Investigating Nonlinear Solvatochromism in Perylene



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Abstract

Document Sections

- I. Introduction
- II. Experimental Section
- III. Results and Discussion
- IV. Conclusion

Authors

Figures

References

Keywords

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Perylene is an organic compound with potential for different optical applications. One important factor that influences the linear responses of organic molecules is the solvent used in the solution. The nonlinear solvatochromism, however, is not as well explored. Thus, we investigate the nonlinear properties alongside photophysical parameters for perylene in toluene, dichloromethane, and chloroform. The two-photon absorption (2PA) spectra (550-800 nm) were obtained by the femtosecond Z -scan technique. A single 2PA band (~25 GM) was observed for all molecules, around 600 nm. Such results indicate minimal variations in the 2PA with different solvents for pure perylene.

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Abstract—Perylene is an organic compound with potential for different optical applications. One important factor that influences the linear responses of organic molecules is the solvent used in the solution. The nonlinear solvatochromism, however, is not as well explored. Thus, we investigate the nonlinear properties alongside photophysical parameters for perylene in toluene, dichloromethane, and chloroform. The two-photon absorption (2PA) spectra (550-800 nm) were obtained by the femtosecond Z-scan technique. A single 2PA band (~25 GM) was observed for all molecules, around 600 nm. Such results indicate minimal variations in the 2PA with different solvents for pure perylene.

Keywords - Perylene, two-photon absorption, solvatochromism, open-aperture Z-scan.

I. INTRODUCTION

Organic compounds exhibit intriguing optical properties, including significant nonlinear optical responses (NLO) [5], due to the presence of π -conjugated structures that promote efficient charge delocalization. Therefore, they are promising candidates for developing new devices and applications involving nonlinear processes, which range from biological imaging techniques based on second-harmonic generation (SHG) [2], photodynamic therapy [3], optical limiting [4], and optical frequency converters [5].

Currently, there is growing interest in smaller organic compounds because they possess well-defined transition dipole moments and are easily engineered [6]. One promising organic molecule is perylene, known for its emissive properties that can be utilized in various applications, including dye lasers, photovoltaics, and random lasers, among others. Perylene and its derivatives have also been reported to exhibit huge two-photon absorption cross-sections (σ^{2PA}) [7], a third-order nonlinear optical process, related to the third-order susceptibility ($\chi^{(3)}$).

However, it is important to consider factors that influence nonlinear responses, such as the choice of solvent. Studies on solvent effects in linear spectroscopy across various species indicate that the solute interacts with the medium in diverse ways, resulting in changes in polarity, dielectric constant, or polarizability of the surrounding medium. Solute-solvent interactions may be non-specific, described in terms of van der Waals interactions, and/or specific, such as hydrogen bonding or electron donor/acceptor interactions. Given this, the influence of solvents on two-photon absorption (2PA) should be examined; however, there is less discussion on this topic compared to linear solvatochromism.

In this work, we focus on the variation of the linear and nonlinear responses of perylene in three different solvents: toluene, dichloromethane, and chloroform. Linear optical measurements, including one-photon absorption (1PA), fluorescence, fluorescence anisotropy, fluorescence quantum yield (ϕ_f), fluorescence lifetime (τ_f), and solvatochromism, were performed. For nonlinear responses, the Z-scan [8] was performed with a femtosecond laser, allowing the determination of σ^{2PA} from 550 to 800 nm.

II. EXPERIMENTAL SECTION

A. Compounds

The commercial perylene (Pn) studied here was acquired from Acrôs Organics company without any further purification (99%+ purity). The compound is a polycyclic aromatic hydrocarbon containing 20 carbon atoms, with the chemical formula $C_{20}H_{12}$. This compound features two aromatic rings connected by a carbon-carbon bond, giving it a flat, centrosymmetric molecular structure and high molecular conjugation [9].

B. Photophysical properties

To determine the photophysical properties of perylene in different solvent media, namely toluene (PnT), chloroform (PnC), and dichloromethane (PnD), solutions were prepared at approximate concentrations of 10^{-4} mol/L and 10^{-2} mol/L to perform linear and nonlinear optical measurements, respectively. The 1PA measurement was recorded using a UV-Vis spectrophotometer (Shimadzu, model UV-1800), with the sample placed in a quartz cell with a 2 mm optical path. The fluorescence emission and fluorescence anisotropy measurements were obtained using a fluorometer (Hitachi, model F-7000) and a quartz cell with a 10 mm optical path. ϕ_f of perylene was determined by the Brouwer method [10], exciting at 370 nm. Here, Coumarin 450 dissolved in ethanol ($\phi_f^{\text{ref}} = 80\%$) was used as the standard sample [11]. τ_f was determined using the time-resolved fluorescence technique, employing a Pharos laser system (Light Conversion, model PHAROS-PH1, ~237 fs, 300 Hz). The sample was excited at 343 nm (1030 nm third harmonic), and the fluorescence signal was monitored as a function of time. For more details on the technique, see the following references [12].

Using the solvatochromic correlation, we estimate the difference in the permanent dipole moment between the first excited state and the ground one ($\Delta\vec{\mu}_{01} = \vec{\mu}_{11} - \vec{\mu}_{00}$, in

Debye), which could give further information on the excited state and the solvent's impact. For this, Bakhshiev equation was employed, given by [13]: $\frac{\Delta\bar{\nu}}{\Delta F_B} = \frac{2}{hca^3} |\Delta\vec{\mu}_{01}|^2$, where $\Delta\bar{\nu} = \bar{\nu}_{abs} - \bar{\nu}_f$ (in cm^{-1}), $\Delta F_B = \frac{2n^2+1}{n^2+2} \left(\frac{\epsilon_r-1}{\epsilon_r+2} - \frac{n^2-1}{n^2+2} \right)$ is the Bakhshiev polarity function, h is Planck's constant, c is the light speed, and a is the solvent cavity radius. a was estimated using the Einstein-Smoluchowski equation [14]: $a^3 = \frac{3}{4\pi} \frac{\tau_{fl}KT}{\eta \left(\frac{0.4}{r} - 1 \right)}$ where r is the anisotropy coefficient, K is the Boltzmann constant, T is the room temperature, and η is the solvent viscosity coefficient.

C. Two-photon absorption measurements

The σ^{2PA} measurements of PnT, PnD, and PnC were performed using the well-established open-aperture Z-scan technique [8]. The experimental setup used to determine σ^{2PA} includes a laser system (Light Conversion, model Pharos-PH1, 1030 nm, 750 Hz). This laser system is used to pump an optical parametric amplifier (Light Conversion, model ORPHEUS), producing laser pulses ranging from 150 to 180 fs, from 220 nm to 3000 nm. σ^{2PA} of perylene was investigated in the range of 550 nm to 800 nm, with a 10 nm spectral resolution. Transmittance was recorded using a silicon photodetector coupled to a lock-in amplifier, which was triggered at the laser system repetition rate. For further details, see ref [15].

III. RESULTS AND DISCUSSION

A. Linear Characterization

Figure 1a shows the 1PA spectrum (blue line) obtained for PnT with three well-separated peaks related to the vibrational progression of the molecule at 390 nm (3.18 eV), 412 nm (3.01 eV), and 439 nm (2.82 eV). For the other two cases, the 1PA spectra of PnC (cyan line, Fig. 1a) and PnD (yellow line, Fig. 1c) are similar, presenting the three peaks at 389 nm, 411 nm, and 438 nm, showing a small hypsochromic (blue) shift when compared with PnT. In the lowest energy peak, the molar absorptivity presented its highest value of $3.25 \times 10^4 \text{ L.mol}^{-1}\text{cm}^{-1}$ for PnT, $3.59 \times 10^4 \text{ L.mol}^{-1}\text{cm}^{-1}$ for PnD, and $3.19 \times 10^4 \text{ L.mol}^{-1}\text{cm}^{-1}$ for PnC. This difference can be attributed to the polarity of the solvents, leading to a blueshift in the chlorinated solvents. From the anisotropy coefficient ($r(\lambda)$) (Fig. 1a, red points), it was observed that within the absorption band (450-350 nm), the behavior was approximately constant (0.01, -0.003, and 0.002 for PnT, PnD, and PnC, respectively), thereby corroborating the initial hypothesis that the multiple peaks are related to the same electronic state (S_0 - S_1). The negative value for DCM may be ascribed to a greater diffuse rotation process compared to the other solvents, since DCM has the lowest viscosity.

Figure 1b also shows the fluorescence emission spectra for all three solutions (425 nm to 550 nm, excited at 300 nm). The difference between the highest fluorescence peak and the lower energy absorption was approximately 12 nm, indicating a low Stokes shift and no difference between the solutions, suggesting the absence of specific solute-solvent interactions and a small charge transfer transition [16], which can be explained by the molecule's centrosymmetric nature [17,18]. Additionally, the results

showed not only a decrease in the molecular transition energy (redshift), but also a slight decrease in the fluorescence intensity of the second peak of the solution with chlorinated solvents when compared with toluene, suggesting greater stabilization of the excited state in more polar solvents [18]. All spectra agree with those observed in the literature [19,20].

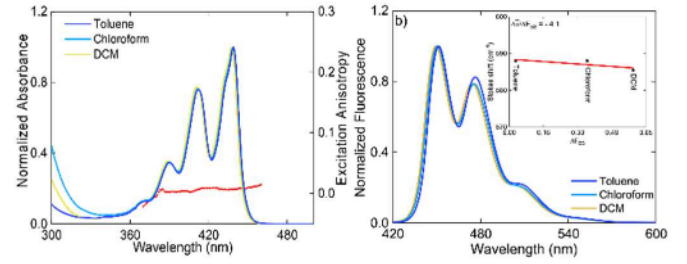


Fig. 1. a) 1PA spectra of PnT (blue line), PnD (yellow line), and PnC (cyan line). The anisotropy scale ranges from -0.1 to 0.15 (red dots). b) Fluorescence emission of PnT (blue line), PnD (yellow line), and PnC (cyan line). The inset linear regression of the graph of the Stokes shift vs. the Onsager polarizability function.

Upon analysis of the results in Table 1, a decrease in Φ was observed with solvent polarity, which indicates a solvatochemical effect [15]. The PnT shows a high Φ of approximately 53%, which is consistent with its low non-radiative rate (k_{nr}). For large non-radiative processes, fluorescence decreases and, consequently, Φ is reduced. The relatively low Φ value for PnC can be explained by the anisotropy value very close to zero ($r = -0.01$), which is associated with a diffusive rotation process that increases the non-radiative rate. Table 1 also shows τ_{fl} of the solutions, in which PnT had the highest value and PnC the lowest. The results show that chlorinated solvents have similar τ_{fl} , and that decreases with solvent polarity. The difference between τ_{fl} can be explained by the distinct non-radiative decay rates that increase for chlorinated solvents [19].

Table 1. Photophysical properties for all the different perylene samples

Molecule	PnT	PnD	PnC
$\tau(\text{ns})$	4.7 ± 0.5	3.9 ± 0.3	3.5 ± 0.5
$\Phi\%$	53 ± 4	52 ± 3	49 ± 2
$k_{nr}(\text{ns}^{-1})$	0.10 ± 0.01	0.12 ± 0.02	0.14 ± 0.02
$a^3(\text{\AA})$	210 ± 21	64 ± 4	32 ± 4
$\Delta\mu_{01}(D)$	0.09 ± 0.04	0.05 ± 0.03	0.04 ± 0.02

The calculated value of the Onsager cubic radius (a^3) for PnT, PnD, and PnC allows determining $|\Delta\vec{\mu}_{01}|$ (Table 1). The small values demonstrated that the excited state has a permanent dipole moment slightly larger than the ground state. This difference indicates that the molecule is slightly more polar in the excited state. Therefore, the solvent-solute interaction should be slightly stronger in the excited state [16,18]. Besides that, the $\Delta\vec{\mu}_{01}$ remained the same in all solvents, within experimental error, indicating no influence of the solvent on the electronic distribution in the excited state.

B. Two-photon absorption.

The open circles in Fig. 2 represent the σ^{2PA} spectra for PnT, PnD, and PnC. σ^{2PA} , determined from the Z-scan curves, were evaluated for the wavelength range 550-800 nm, equivalent to the 275-400 nm 1PA range, allowing the 2PA study in different spectral regions. The normalized linear absorption spectra in Fig. 2 (solid blue lines) are displayed to study the 1PA and 2PA of the solutions. For PnT (Fig. 2a), a single band is observed in the 2PA spectrum between 570 nm

and 670 nm, which is related to the linear spectrum between 285 nm and 335 nm. The 2PA band is located in a different region than the 1PA one because perylene is a centrosymmetric molecule, such that states allowed by 2PA will be forbidden by 1PA [21]. It can also be seen that the vibronic progression for all solutions, clear in the linear absorption spectrum, does not appear in the 2PA spectrum.

The highest σ^{2PA} observed was around 27 GM at 640 nm (1.94 eV), which is considered a modest value, due to the short π -chain conjugation and the absence of electron acceptor and/or donor groups [6]. For PnD (Fig. 2b), the 2PA band is in the same region and magnitude as for PnT. However, for PnC, it can be observed that the 2PA spectrum exhibits a slight shift compared to the other two, with the highest value of 24 GM at 610 nm (2.03 eV). There is a resonant enhancement as the 2PA excitation approaches the 1PA band. Although a slightly hypsochromic shift in the maximum σ^{2PA} wavelength of PnC, there were no visible changes in the spectra, within experimental error, with the change of solvent polarity. These could be related to the lack of more polar solvents that could lead to a bigger change than observed here, or the molecule presenting a zero permanent dipole moment. Therefore, the increase in the σ^{2PA} and a possible shift of the band, visible in other studies [22], was not possible in this case, due to the lower solvent interaction.

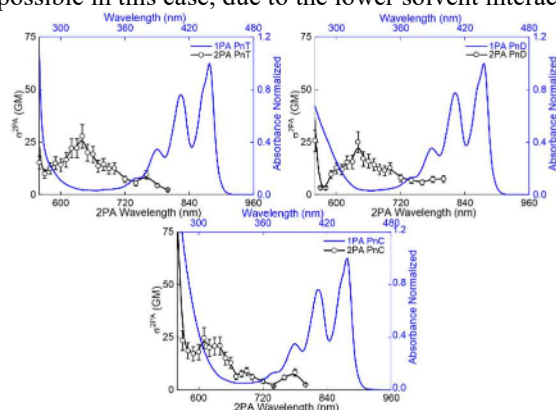


Fig. 2. Linear absorption and σ^{2PA} spectra (black line and dotted line, respectively) for a) PnT, b) PnD, and c) PnC.

IV. CONCLUSION

Although the interaction between solute and solvent affects photophysical properties, further research is needed in nonlinear optics. The results presented here are relevant for enhancing the understanding of nonlinear solvatochromism, particularly regarding the impact of the solvent on two-photon absorption. No significant influence on linear properties or on σ^{2PA} has been observed here, which can be explained by the small molecular size and its centrosymmetric and planar structure with small interactions with the solvent. Therefore, the study of molecular systems presenting donor/acceptor groups and with other symmetries is important to reveal aspects related to the solvent interaction in nonlinear optics.

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