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Synthesis, Spectroscopic Characterization, Photophysical Properties of N,-(5-amin-1, 10-phenanthroline) perylene-3, 4, 9, 10-tetracarboximonoimide

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Abstract: *The synthesis and optical, electrochemical, and electronic properties of N,-(5-amin-1,10-phenanthroline)perylene-3,4,9,10-tetracarboximonoimide [pPDI] are reported. The molecular structure of the compound was elucidated by FTIR, mass spectrometry, elemental analysis (CHN), and DFT calculations. Their optical and electrochemical properties were investigated by absorption and fluorescence spectroscopy and cyclic voltammetry. Spectroscopic and electrochemical studies for pPDI show that phenanthroline coordination does not affect the optical and electrochemical properties of the perylene monoimide ligand.*

Keywords:*dye,organic synthesis, perylene tetracarboxylic, absorption, luminescence*

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I. Introduction

Scientific and technological interest in compounds deriving from 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) has increased lately due to their properties, such as high thermal and photochemical stability and high absorption in the visible region (400-600 nm)[1-3]. Some of these compounds, such asPDIs (perylene-3,4:9,10-tetracarboxylic acid derivatives),have been shown to increase physical and chemical adsorption onto the electrode surface by means of non-covalent π-π stacking interaction[4-9].

The unique photophysical and photochemical properties of perylene derivatives enable them to be used, among other applications, in photo-induced energy and/or electron organic transfer systems, as semiconductor materials for electrophotography, in organic photovoltaic devices for converting solar energy, electronics, and photosensitizers[5-12].Perylene moieties may exhibit electron donor or acceptor properties, depending on the nature of the side substituents [10-12]. For instance, the phenanthroline or terpyridine fractions of these PDIs provide attachment points for transition metal-based multielectron catalysts [13].In some cases, because of their rigid-rod nature, perylene-based structures can serve as standards for steady-state fluorescence anisotropy. In addition, some PDIs exhibit self-assembly and aggregation properties, which facilitates light harvesting and high-efficiency energy transfer.

In view of the importance of perylene derivatives, this article aims to present the synthesis, characterization, and linear photophysical and nonlinear optical properties of N,-(5-amin-1,10-phenanthroline)perylene-3,4,9,10-tetracarboximonoimide (henceforth referred as thepPDI).

II. Experimental

2.1 Materials

Both the synthesis of the pPDIand the preparation of solutions for electrochemical and spectroscopic assays were done under O_2 atmosphere. Quinoline (a product of Sigma Aldrich) was distilled twice under reduced pressure. Perylene-3,4,9,10-tetracarboxylic dianhydride, zinc acetate, 5-amine-1,10-phenanthroline, and tetrabutylammonium hexafluorophosphate were also obtained from Aldrich and used without further purification. HPLC grade solvents were distilled just before being used in spectroscopy.

2.2 Characterization techniques

CHN elemental analysis of the pPDI was performed on an EA 1110 CHNS-O Carlo Erba Instrument. FTIR spectra were recorded on a Bomem-Michelson 102 spectrometer in solid state using KBr pellets within the 4000-400 cm^{-1}range.

The electronic absorption spectrum was recorded on an Agilent 8453A UV-vis spectrophotometer or on a Jasco V-660 UV-vis spectrophotometer.

The electrochemical behavior of the pPDIin DMF at the scanning rate at different scan rates 25, 50, 100 e 200 mV $s^{-1}$was investigated by cyclic voltammetry in order to evaluate the reduction and oxidation potentials. Voltammetric measurements were carried out with a µAutolab Type III potentiostat at 25°C deprived oflight. Glassy carbon electrode was employed as working electrode (d = 2 mm), Pt electrode as counter electrode (d = 4 mm), Ag/AgCl electrode as reference electrode, ferrocene as internal reference electrode and $TBAPF_6$(0.1 M) as supporting electrolyte. The concentration of the DMF solutions used to perform cyclic voltammetry measurements of synthesized pPDI was 10^{-3} mol L^{-1}.

The luminescence spectrum was recorded on a Shimadzu RF-5301PC spectrofluorometer or on a Horiba Jobin Yvon Fluorolog 3-22 spectrofluorometer. The concentration used was $1x10^{-5}$ mol L^{-1} (λabs maximum = 0.3), with acetonitrile as solvent.

All computational calculations were performed by means of the Gaussian 09 (G09) program package [14], D.01 edition, employing the DFT method with Becke's three-parameter hybrid functional and Lee-Yang-Parr's gradient corrected correlation functional [14-15] (B3LYP) in combination with LanL2DZ basis set [16]. The ground-state geometry of the pPDI was optimized in gas phase. SCF-tight convergence criteria were used for all optimizations. The solvent DMSO was included in the calculations using the PCM system. The triplet state was obtained using UB3LYP/LANL2DZ. Electronicanalysis was performed using TD-DFT calculations with 40 excited states.

2.3 Synthesis of thepPDI

The literature procedure of the synthesis (Fig. 1) was modified as follows [2-3, 17]: one equivalent 136 mg (0.170 mmol) of perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) was dispersed in freshly distilled quinoline (10 mL) with one equivalent (32.30 mg; 0.170 mmol) of 5-amino-phenanthroline. Then, 10% by weight relative to 5-amino-phenanthroline anhydrous zinc acetate was added, and the solution was heated under nitrogen to 220°C for 12 h. After cooling, three volumes of 1 M HCl were added, and the precipitate was collected and rinsed copiously with water and ether. Afterwards, 150 mL of methanol was added, stirred for 30 min, and allowed to stand for 4 h at -10°C. Next, itwas first washed with a 5% solution of sodium carbonate and, subsequently,with methanol and ether and dried under vacuum (50% yield). Insufficient solubility for NMR; m/z + 3H= 570.2 (Figure S1- Supporting information). Anal. Calcd (found) for pPDI $C_{36}H_{15}N_3O_5$: C, 75.92 (76.36); H, 2.65 (2.92); N, 7.38 (7.32)%.

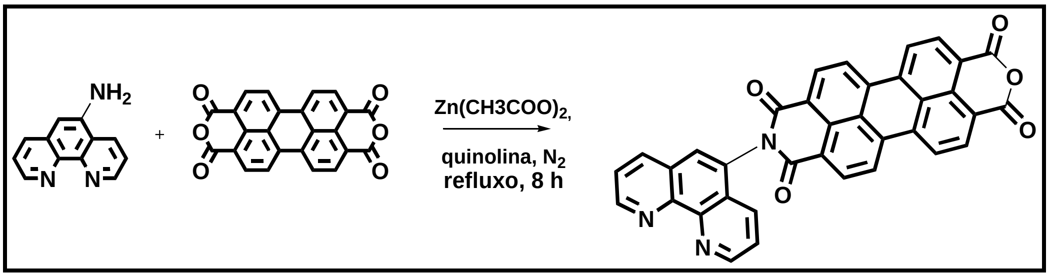

Figure 1: Synthesis of N,-(5-amin-1,10-phenanthroline)perylene-3,4,9,10-tetracarboximonoimide

III. Results And Discussion

3.1. Synthesis and characterization

3.1.1 Structural and Optical Characterization

Our attempts to grow diffraction-quality crystals of the synthesized free ligand (pPDI) was not successful.Therefore, the structural parameters and electronic effects of the pPDI were determined by means of DFT calculations. Figure2 shows the optimized structure for pPDI.

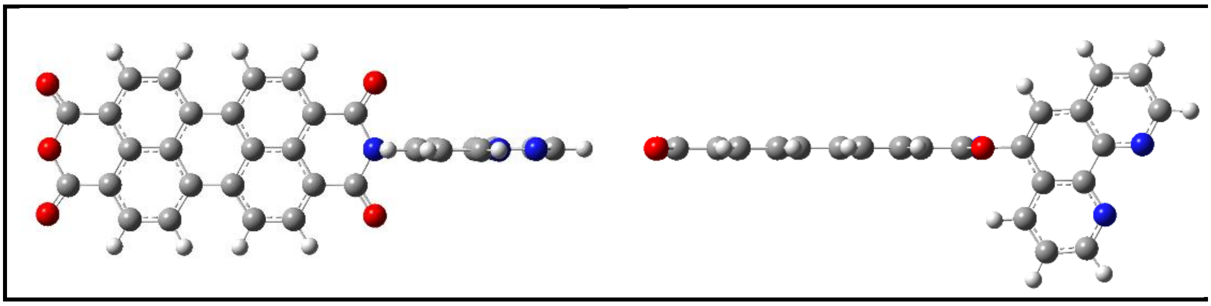

Figure 2: DFT optimized structure of the pPDI in gas phase.

Vibrational modes were obtained ensuring that imaginary frequencies were notgenerated in the minimum structures. The optimized structure of the substituted perylene ligand indicates that perylene is perpendicular to the phenanthroline ligand, and the predicted dihedral angle between phenanthroline and perylene is 89.8°. The energy values of HOMO and LUMO orbitals are shown in Table 1.

Table 1: Values of theoretical energies for the border orbitals.

Orbital	**pPDI**		
	%phen	**%perylene.**	**E (ev)**
L+2	5	95	-2,33
L+1	0	100	-2,44
LUMO	0	100	-3,97
HOMO	0	100	-6,37
H-1	40	60	-6,9
H-2	48	52	-7,01

The contribution percentages of each component of the pPDIHOMOs (H-1 and H-2) and LUMOs (L-1 and L-2) orbitals indicate that the border orbitals (HOMO and LUMO) have 100% of perylene chromophore. This behavioris confirmed byelectrochemistry values for thepPDI, in which the lower energy oxidation and reduction processes refer to perylene only. Some perylene derivatives (PDIs) exhibit high reduction potential related to the phenanthroline group(~ -1.7 V vs SCE).Therefore, their contribution occurs only at higher-energy LUMOs. The difference (ΔE) between theoretical LUMO and HOMO values forthe pPDIis 2.40 eV, close to the experimental value (2.27 eV), which atteststo the reliability of the theoretical calculations.

3.1.2Cyclicvoltammetry

Figure 3 shows the cyclic voltammogram of the pPDI in DMF solution. The voltammetric curves indicate that the pPDI undergoes one reversible one-electron reduction process (E½ = -0.54 V) vs Ag/AgCl and one irreversible reduction process (E½ = -0.015) Vs Ag/AgCl based on the perylene core. These processes were assigned to the anion radical ($pPDI/PDIp^{\bullet-}$) and dianion radical ($PDIp\bullet-/PDIp^{-2}$) moieties of the pPDI, respectively, as reported for other perylene derivatives [3, 23-24].

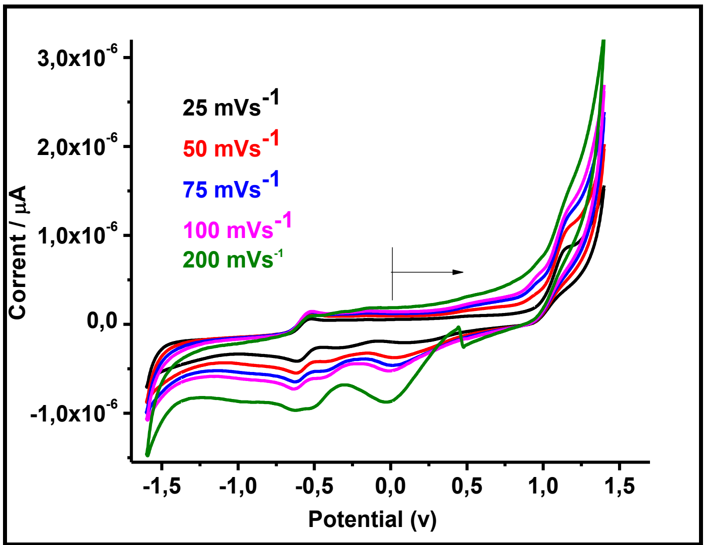

Figure 3: Cyclic voltammogram of 1×10^{-3} M of pPDI in DMF/0.1 M $TBAPF_6$. The scan rates at increasing peak current intensities are 25, 50, 75, 100, and 200 mV^{-1}.

ThepPDI exhibits one reversible oxidation process at 1.14 V (ΔEp = 210mv) corresponding to the radical cation formation, $PDIp^{\bullet+}$. When voltammograms are compared, it is possible to observe that the current density decreases at the lowest velocity, indicating that oxidation is less favored at that point. This, in turn, suggests that the cation radical undergoes to a slow decomposition, causing the compound to adsorb onto the electrode [17, 25].

3.1.3 IR Spectra

The experimental IR spectrum for the pPDI (Fig.4) isconsistent with the proposed asymmetrical functionalization of perylene [18] and matches the theoretical IR (figure shown in the supporting information S2).

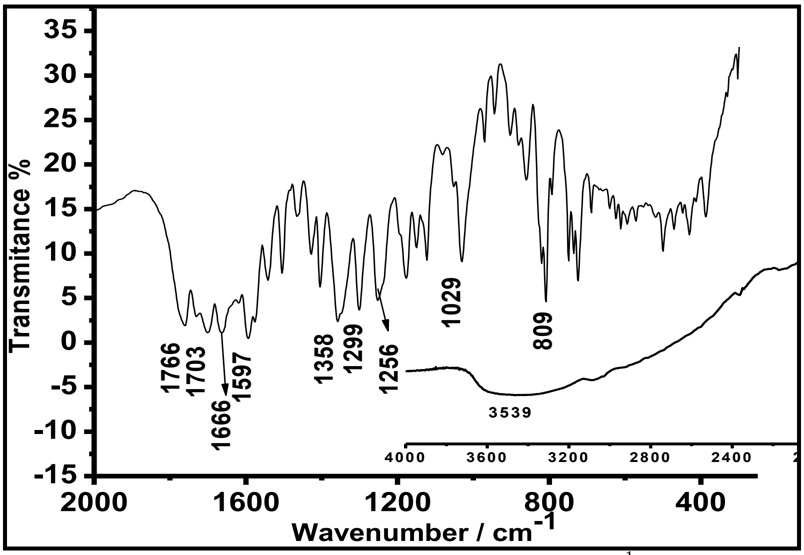

Figure 4: IR spectrum for the pPDI in KBr pellets in the range of 2000-400 cm^{-1} and 4000-2000 cm^{-1} (inset).

Regarding tothe pPDI, the absorption band at 1766 cm^{-1} refers to the carbonyl anhydride stretch and the bands at 1703 and 1666 cm^{-1} correspond to νC-O stretches of the imide group [2-3,1-20]. The band at 1029 cm^{-1} refers to the νC-O-C stretch ofanhydride whereas the band at 1358 cm^{-1} corresponds to νC-N amine formed by the oxygen atom of anhydride when replaced by the nitrogen atom of phenanthroline, which indicates that phenanthroline was functionalized in only one side of perylene [19-20]. The pPDI exhibited strong intermolecular hydrogen bonding, which is characterized by a broad and irregular-shaped band in the region of approximately 3500-2000 cm^{-1}. The bands at 1609, 1597, 809, 680, and 771 cm^{-1} are attributed to the aromatic skeleton ring [21].

3.1.4 Absorption in the ground state and luminescence

The pPDIabsorption spectrum was obtained using diluted DMSO solutions (5.0×10^{-6} mol l^{-1}) and PTCDA in alkaline medium (pH=12), as seen in Figure 5. The UV-vis spectrum of the pPDI exhibits a broad band with three distinct maximums at 527 nm(ε = 18735L mol^{-1} cm^{-1}), 493 nm (ε = 15880L mol^{-1} cm^{-1}), and 463 nm (ε = 8190 L mol^{-1} cm^{-1}), attributed to π- π* electronic transitions of the perylenedye [3, 15-21].The band at 380 nmrefers to the contribution of the phenanthroline group to the ILCT transition.

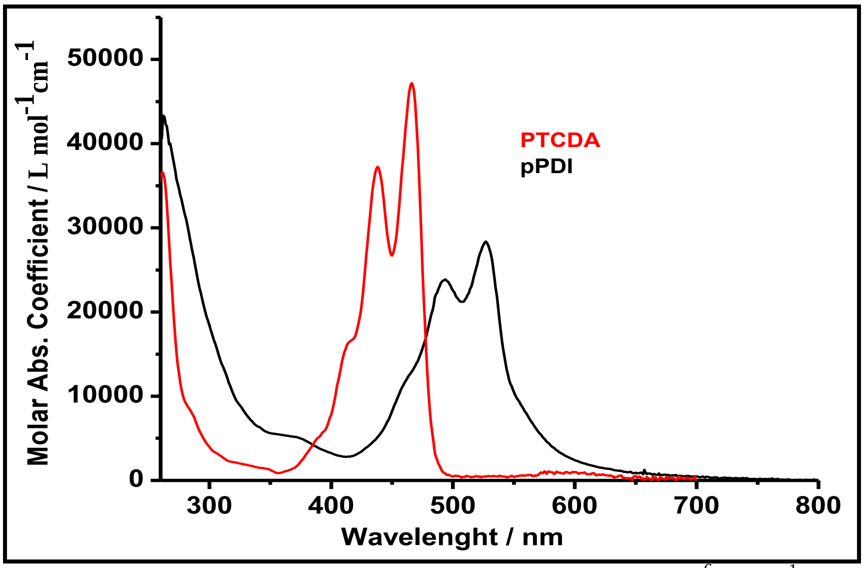

Figure 5:UV-vis absorption spectrum in the range of 350-700 nm for a 5.0 × 10^{-6} mol L^{-1} solution of the pPDI in DMSO at 25°C

As to the absorption spectrum of the PTCDA precursor in alkaline medium, a shift was observed for higher wavelengths. This result opens the possibility for pPDI to act as photosensitizers. This shift suggests an increase in perylene conjugation when binding to 5-amino-phenanthroline occurs, causing a decrease in the

HOMO-LUMO GAP of the pPDI[22].The theoretical electronic spectrum of the pPDI ligand shows a band at λ_{max} = 555 nm assigned to $\pi_{pery} \rightarrow \pi^*_{pery}$ transition (100% HOMO→LUMO) entirely located on the perylene ring.

Figure 6 shows the absorption spectrum of thepPDI in different solvents. With regard to polar protic solvents, e.g., methanol, it is possible to observe that spectra exhibit loss of vibrational structure (peak at 480 nm). This phenomenon may be associated withthe interaction between OH and NH groups of the solvents and the PDI1[17].

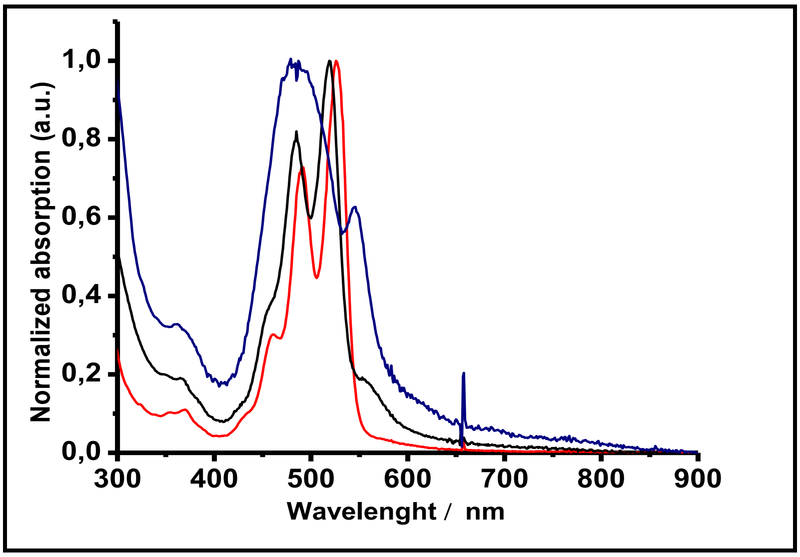

Figure 6: Normalized Absorption spectra of thepPDI in solvents of different polarities: DMF (red), acetonitrile (black), and methanol (blue) in the range of 300-900 nm.

Table 2 presents electronic transitions of greater oscillator force for the pPDI obtained by theoretical calculations. The lower-energy transitions (256 nm and 258 nm), predominant in electron absorption spectra, are related to perylene-perylene intraligandtransitions(π→π*). At 261 nm and 281 nm, the transitions are also intraligand type with a mixture of phenanthroline/perylene orbitals. Finally, the band of higher oscillator strength (555 nm) is attributed to the perylene→perylene HOMO→LUMO transition (π→π*).

Most of the perylene derivative compounds and the PTCDA precursor itself are known to have low solubility in organic solvents and to be insoluble in aqueous solution (typically 1-2 mg L^{-1}) [7,20]. PTCDA showed DMSO solubility of 0.001 g L^{-1} while pPDI obtained solubility,higher than PTCDA, about 0.33 g L^{-1} in DMSO.

Table 2: Values of λ (nm), oscillator force (f), dominant transitions (percentage of contributions) and assignments for the pPDI.

λ (nm)	f	Percentage of Contributions	Assignment
555	0.9929	HOMO→LUMO (100%)	perylene→ perylene (100%)
488	0.0038	H-1→LUMO (99%)	[perylene/phenanthroline (60%, 40%)]→perylene (99%)
385	0.0026	H-5→LUMO (69%), H-4→LUMO (17%)	perylene→perylene (69%)
360	0.0802	H-7→LUMO (76%), HOMO→L+2 (15%)	perylene→perylene (76%)
321	0.001	HOMO→L+3 (99%)	perylene→perylene (99%)
288	0.2553	H-2→L+2 (36%), H-1→L+3 (37%)	[perylene/phenanthroline (52%/ 48%)]→L+2 (36%), [perylene/phenanthroline (60%, 40%)]→L+3 (37%)
306	0.0018	H-1→L+1 (69%), HOMO→L+4 (16%)	[perylene/phenanthroline (60%, 40%)]→ perylene (100%)] (69%), perylene→ [perylene; phenanthroline (56%, 44%)] (16%)
302	0.0021	H-3→L+3 (25%), H-1→L+4 (41%), HOMO→L+4 (25%)	[perylene/phenanthroline (60%/ 40%)]→ perylene→perylene / phenanthroline (56%,44%)] (66%)
293	0.0011	HOMO→L+5 (80%)	perylene→perylene (80%)
281	0.0035	H-2→L+2 (99%)	[perylene/phenanthroline (52%/ 48%)]→L+2 (99%)
261	0.242	H-3→L+3 (48%), H-1→L+4 (35%)	[perylene/phenanthroline (68%/32%)]→[perylene/phenanthroline (65%/35%)] (48%), [perylene/phenanthroline (60%/ 40%)] →[perylene/phenanthroline (56%/ 44%)] (35%)
259	0.012	H-5→L+2 (61%), HOMO→L+8 (23%)	perylene→perylene (61%)
256	0.066	H-16→LUMO (70%), HOMO→L+6 (12%)	perylene→perylene (12%)

Under excitation at 490 nm, the pPDI exhibits a broadband emission with maximum at 584 nm and three distinct peaks (Fig. 7), assigned the ILCT transitions of the perylene group with λ_{max} at 558, 584, and 635 nm, corresponding to (0 ← 0), (0 ← 1) and (0 ← 2), respectively[3, 21, 26, 48-51, 53-56].

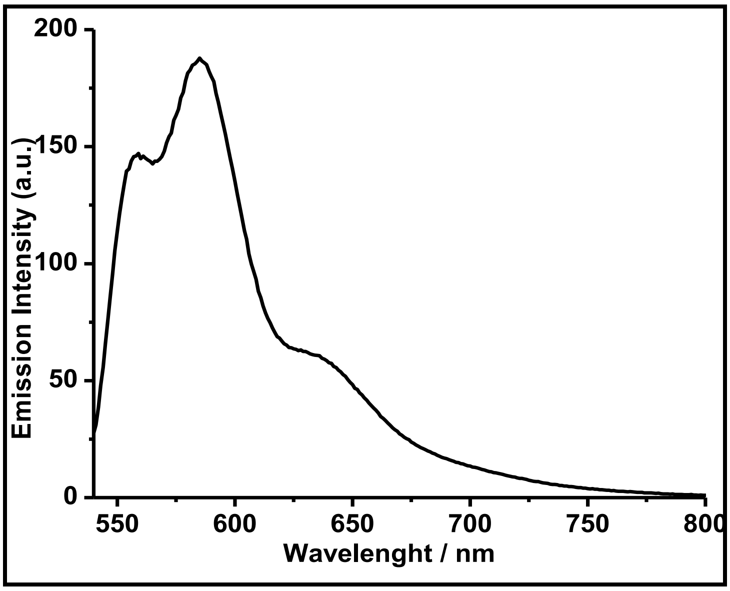

Figure 7: Emission spectra of the pPDIin DMSOsolvent in the 500-800 nm region, λ_{exc} = 490 nm at 25°C.

3.1.5 Optical properties of the dye

Luminescence spectra of the pPDIwere obtainedat differentconcentrations, as shown in Figure8. In general, when the fluorophore solution is diluted, the observed emission can be attributed to the isolated molecule. However, with increasing concentration, several types of processes that alter its spectral profile may occur, such as theformation of dimers in the fundamental electronic state, shown in absorption spectra as bands in the red region [26, 27].

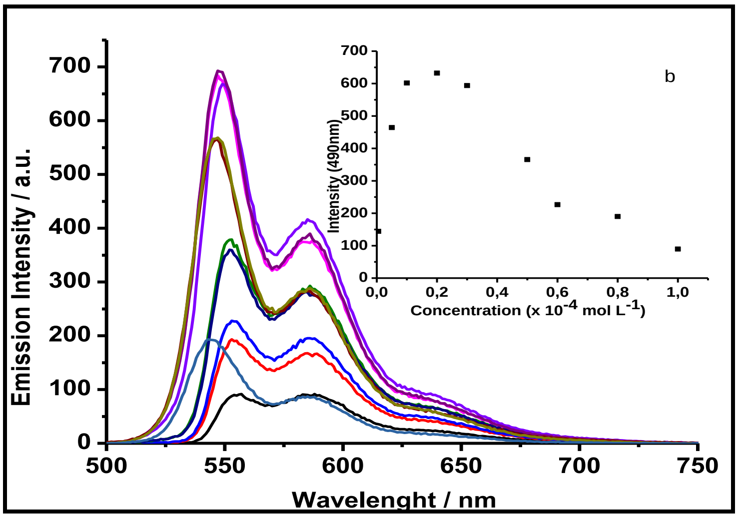

Figure 3: Plotting of luminescence measurements versus concentration of pPDI in DMF.

Weak interactions occurin the structure of free perylene tetracarboxylic diimide, promoting the self-organization of the molecules by means of a hydrophobic effect, which is minimized in organic solvents, and,especially, by the overlapping of π-π* orbitals between the aromatic rings, fostering the aggregation of the molecules. At diluted concentrations, pPDIs are predominantly found as free monomers. As concentration increases, so do intermolecular interactionspromotingthe self-organization of molecules (Wei Wang, 2003).

We observed that emission intensity increases up to 2.0×10^{-4} M pPDI concentration. At higher concentrations, emission intensity decreases, which is likely due to the self-suppression effect, not uncommon toseveral PDIs [26-27].

IV. Conclusion

This study presents the synthesis and characterization of a perylene derivative compound. This compound exhibits stability in presence of light, and itdoes not present photochemical sensitivity.Theoretical calculation enabled us to obtain the optimized structure of the compound, indicating that perylene and phenanthroline are on different planes. In addition, the pPDI under investigation has high absorption in the region of visible light and better solubility when compared to PTCDA, two important characteristics for the various applications of perylene derivatives.These characteristics make the PTCDA compost a candidate to act as a photosensitizer in photochemical reactions, such as transfer of electrons and energy, in synthesis of coordination compounds, among others.

Acknowledgements

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Supporting information

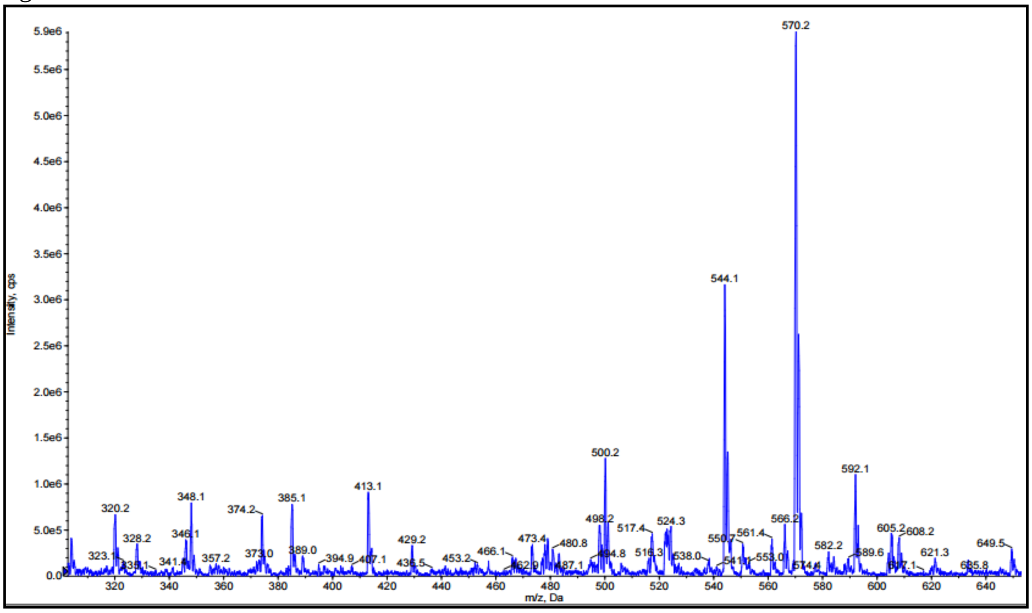

Figure S1: Mass spectrum of thepPDI in DMSO at 25°C ± 1.

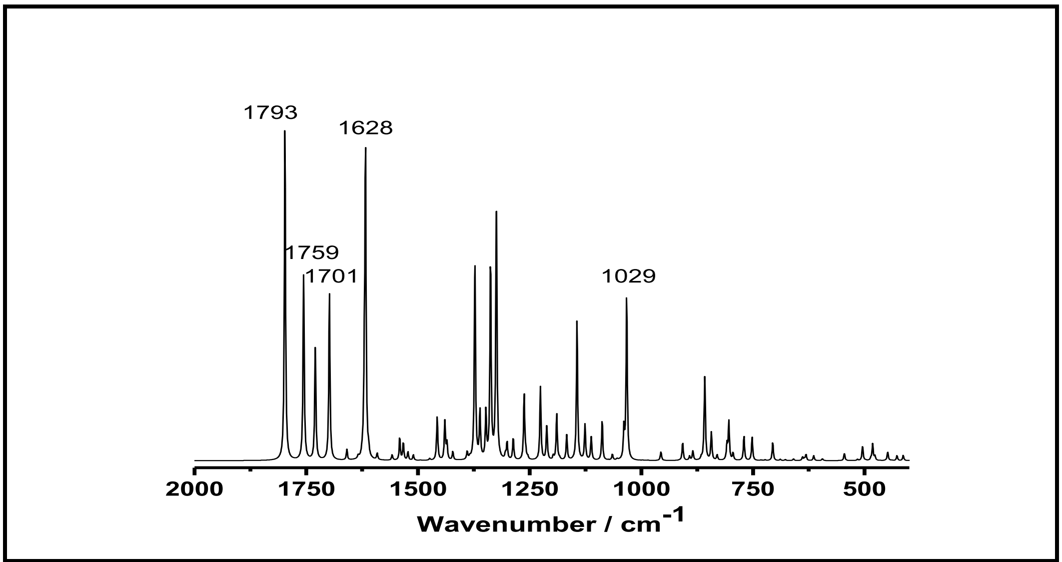

Figure S2: Infrared theoretical of pPDI in the range 4000-400 cm^{-1}.

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