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New long-chain donor-acceptor-donor pyromellitic diimide (PMDI) derivatives. A combined theoretical and experimental study

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ABSTRACT

This study involves the electrochemical, thermal and photophysical profiling of new pyromellitic diimide (PMDI) derivatives containing alkyl chains of different sizes. The photophysical investigation shows that all compounds exhibited absorption in the UV-B region (~290 nm). The band-gaps were calculated by onset peak values of around 4.03 eV. The compounds are photoactive in the UV-A region (312-328 nm) with a small solvatochromic effect in the excited state ($\Delta\lambda_{em}$ =16 nm). The electrochemical studies revealed that the reduction of

the bisimide moiety showed two waves due to the formation of both the radical anion and a dianion. On the other hand, oxidation showed two waves due to the formation of radical cations and dications. The thermal properties were measured by differential thermal analysis (DTA) and thermogravimetric analysis (TGA), and the materials showed high thermal stability ($T_d > 300^{\circ}$ C). Theoretical calculations were also performed to study the geometry and charge distribution of these compounds in their ground and excited electronic states. No significant changes in the absorption and emission maxima were found by changing the solvent or substituents attached to the PMDI structure.

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1. Introduction

Renewable energy (RE) technologies are becoming more and more relevant in the modern society due to the increasing energy demands. Unlike fossil fuelbased energy sources, RE sources help in decreasing environmental pollution and greenhouse gas [1]. In addition, RE sources, such as photovoltaics (PVs), wind, thermal, solar, hydropower, and biomass, are reliable and sustainable sources to meet the rising energy demands [2]. In this context, PV is attractive technology for the direct conversion of sunlight into electricity with an approximate efficiency of up to 25%. However, its use is restricted due to their high production and environmental costs since some solar cells are based on silicon [3]. The development of new technologies, such as dye-sensitized solar cells (DSSCs) [4], organic PVs [5], perovskite PVs [6], and inorganic quantum dot solar cells [7] have the potential to enhance energy conversion efficiency at lower costs [8]. Dye-sensitized solar cells (DSSCs) also called Grätzel cells [9], are PV devices that uses less expensive materials than those used in conventional silicon solar cells. Furthermore, the fabrication process for DSSCs are simpler [10], thus generating cost-effective PV devices [1] that show approximately 13% efficiency [11]. DSSCs are promising PV devices due to the relative low cost of materials, their easy manufacture and advantages related to

mechanical flexibility [12]. transparency, color and In this regard. photosensitizers, a key component of DSSCs, play an crucial role in light harvesting. To date, a wide variety of different dyes, e.g., metal-free organic dyes, zinc porphyrin dyes and ruthenium-based dyes, have been developed and widely investigated [13,14]. However, in view of cost and environmental problems associated with metal-based dyes, metal-free dyes are strongly preferred. In last few years, there is increasing research interest in the development of new organic sensitizers and reasonable power conversion efficiencies by them [15,16]. In this context, pyromellitic diimides (PMDI) derivatives dyes have been drawing attention because of their excellent photochemical, thermal and chemical stabilities and low cost production that make them promising candidates for DSSC applications.

The structures of pyromellitic diimides (PMDI), which have the smallest perylene core, have low-lying LUMO energies; however, they also have limited molecular area for intermolecular π overlap [17]. This feature makes them applicable as building blocks for insulating aromatic polyimides for advanced applications ranging from communications to aerospace technologies [18-22].

Therefore, in this work we report the synthesis, thermal, electrochemical and photophysical characterization of PMDI derivatives, which contains alkyl groups with different chain lengths. In addition, to study the geometry and charge distribution of these compounds theoretical calculations were performed in their ground and excited electronic states.

2 EXPERIMENTAL

2.1 Materials and methods

All reagents were purchased from commercial sources and utilized without any further purification. The solvents were purified according to standard procedures [23]. Infrared spectra were recorded on a IRPrestige-21 Spectrophotometer (Shimadzu) using KBr pellets. Proton and Carbon nuclear magnetic resonance spectra (¹H and ¹³C NMR) were recorded in CDCl₃ at 400 and 100 MHz, respectively. Chemical shifts (δ) are reported in ppm referenced to the TMS, and the coupling constants (*J*) in Hertz (Hz). In the photophysical studies, spectroscopic grade solvents were used. The UV-Vis absorption spectra in solution were recorded on a Shimadzu UV-2450 spectrophotometer, and the

steady-state fluorescence spectra were acquired on a Shimadzu RF-5301PC spectrofluorometer. For compounds 6a-c, UV-Vis absorption and fluorescence emission spectra were recorded in THF ($\sim 10^{-5}$ M) and CH₂Cl₂ (DCM) ($\sim 10^{-5}$ M). The guantum yield of fluorescence (FFL) was obtained by applying the dilute optical method. Quinine sulfate (QS) in H₂SO₄ (0.5 mol L⁻¹) (Φ_{FI} =0.55) was used as a standard for the quantum yield [24]. The uncertainties associated to the quantum yield of fluorescence ($\Delta \Phi_{FI}$) measurements using QS are on the order of 6% [25,26]. The electrochemical measurements were accomplished with a DropSens potentiostat (STAT 400). The cyclic voltammetry experiments were performed using 0.1 mg mL⁻¹ solutions of **6a-c** in 0.1 M tetra-*n*-butyl ammonium hexafluorophosphate (TBAPF₆) in dry DCM as the supporting electrolyte, and the ferrocene/ferricenium (Fc/Fc⁺) redox couple as the internal reference. The experiments were conducted using a standard three-electrode cell with a circular glassy carbon electrode, a Pt-wire counter electrode and Ag/Ag^{+} as the reference electrode (AgNO₃ 0.01 M in CH₃CN). The measurements were performed in an electrolyte solution that had been purged with purified nitrogen gas. The spectra of bisimide derivatives 6a-c were potential using obtained at open circuit а Shimadzu UV-1800 spectrofluorophotometer. The thermal properties were examined using differential scanning calorimetry on DSC-50 and SDT Q600 TA instruments using a nitrogen atmosphere with a flow rate of 100 mL min⁻¹ and a heating rate of 10°C min⁻¹. The DSC curves were acquired using two heating-cooling cycles, in order to obtain the thermal transitions and the glass transition temperatures. respectively. Elemental analysis was performed by using a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer System.

2.2. Synthesis

General procedure for the synthesis of 3a-c

4-Acetamidophenol (1) (13 mmol; 2 g), 1-bromooctane (2a) (13 mmol; 3.27 g), potassium carbonate (32 mmol; 4.5 g) and butanone (50 mL) were combined in a two-necked round flask. The mixture was refluxed for 18 h at 70°C. The formed precipitate was removed by vacuum filtration, washed with hot butanone, and recrystallized from MeOH/H₂O. The same procedure was used

for the synthesis of compounds **3b** and **3c** using 1-bromodecane and 1romododecane, respectively.

N-(4-(octyloxy)phenyl)acetamide (3a)

White solid. Yield: 91%. mp.: 104°C. IR (KBr) cm⁻¹: 3272, 2938, 2854, 1650, 1219. ¹H NMR (CDCl₃, 400 MHz) 7.35 (d, 2H, *J*=8.81 Hz); 6.83 (d, 2H, *J*=8.81 Hz); 3.92 (t, 2H, *J*=6.80 Hz); 2.14 (s, 3H); 1.78 (m, 2H); 1.46-1.28 (m, 10H); 0.89 (t, 3H, *J*=6.54 Hz). ¹³C NMR (CDCl₃, 100 MHz) 168.6, 156.0, 130.9, 122.0, 114.8, 68.3, 31.8, 29.4, 26.1, 22.7, 14.1. Elemental Analyses Calcd. for $C_{16}H_{25}NO_2$: C 72.97; H 9.57; N 5.32%. Found: C 73.01; H 9.59; N 5.34%.

N-(4-(decyloxy)phenyl)acetamide (3b)

White solid. Yield: 88%. mp.: 89-93°C. IR (KBr) cm⁻¹: 3220, 2926, 2842, 1640, 1219. ¹H NMR (CDCl₃, 400 MHz) 7.35 (d, 2H, *J*=8.81 Hz); 6.79 (d, 2H, *J*=8.81 Hz); 3.90 (t, 2H, *J*=6.80 Hz); 2.10 (s, 3H); 1.75 (m, 2H); 1.27 (t, 14H); 0.88 (t, 3H, *J*=6.55 Hz). ¹³C NMR (CDCl₃, 100 MHz) 168.7, 156.0, 130.9, 122.0, 114.8, 68.3, 31.9, 29.6, 29.4, 26.1, 24.1, 22.7, 14.1. Elemental Analyses Calcd. for $C_{18}H_{29}NO_2$: C 74.18; H 10.03; N 4.81%. Found: C 74.21; H 10.06; N 4.83%.

N-(4-(dodecyloxy)phenyl)acetamide (3c)

White solid. Yield: 86%. mp.: 99°C. IR (KBr) cm⁻¹: 3310, 2923, 2838, 1652, 1228. ¹H NMR (CDCl₃, 400 MHz) 7.35 (d, 4H, *J*=8.81 Hz); 6.80 (d, 4H, *J*=8.81 Hz); 3.90 (t, 2H, *J*=6.80 Hz); 2.11 (s, 3H); 1.75 (m, 2H); 1.26 (m, 18H); 0.88 (t, 3H, *J*=6.55 Hz). ¹³C NMR (CDCl₃, 100 MHz) 168.5, 156.0, 130.9, 121.9, 114.7, 68.3, 31.9, 29.7, 29.4, 26.1, 22.7, 14.2. Elemental Analyses Calcd. for $C_{20}H_{33}NO_2$: C 75.19; H 10.41; N 4.38%. Found: C 75.23; H 10.44; N 4.41%.

General procedure for the synthesis of 4a-c

N-(4-(Octyloxy)phenyl)acetamide **(3a)** (6.7 mmol; 2 g) was mixed with conc. HCl (37.4 mL) and H₂O (54.6 mL) in a two-necked round flask. The reaction mixture was refluxed for 24 h at 100°C. The reaction was cooled and poured into a solution of NaOH (1 M). The precipitate was removed by filtration, washed with water, and dried under vacuum to afford desired aniline **4a**. The same procedure was used for the synthesis of compounds **4b** and **4c** using *N*-(4-

(decyloxy)phenyl)acetamide or *N*-(4-(dodecyloxy)phenyl)acetamide as precursors, respectively.

4-(octyloxy)aniline (4a)

Rosy solid. Yield: 95%. mp.: 35-39°C. IR (KBr) cm⁻¹: 3401, 2926, 2831, 1518, 1228. ¹H NMR (CDCl₃, 400 MHz) 10.25 (br., 2H); 7.40 (d, 2H, *J*=8.80 Hz); 6.84 (d, 2H, *J*=9.20 Hz); 3.91 (t, 2H, *J*=13.20 Hz); 1.77 (m, 2H); 1.26 (m, 18H); 0.88 (t, 3H, *J*=13.60 Hz). ¹³C NMR (CDCl₃, 100 MHz) 159,3, 124.4, 122,2, 115.5, 68.4, 31.8, 29.4, 26.0, 22.7, 14.1. Elemental Analyses Calcd. for C₁₄H₂₃NO: C 75.97; H 10.47; N 6.33%. Found: C 75.99; H 10.50; N 6.35%.

4-(decyloxy)aniline (4b)

Rosy solid. Yield: 91%. mp.: 108°C. IR (KBr) cm⁻¹: 3407, 2911, 2838, 1504, 1252. ¹H NMR (CDCl₃, 400 MHz) 7.14 (d, 2H, *J*=8.80 Hz); 6.95 (br, 2H); 6.76 (d, 2H, *J*=8.80 Hz); 3.87 (t, 2H, *J*=13.20 Hz); 1.77 (m, 2H); 1.30 (m, 14H); 0.88 (t, 3H, *J*=13.69 Hz). ¹³C NMR (CDCl₃, 100 MHz) 157.1, 127.8, 122.0, 115.5, 68.5, 31.9, 29.6, 26.1, 22.7, 14.1. Elemental Analyses Calcd. for $C_{16}H_{27}NO$: C 77.06; H 10.91; N 5.62%. Found: C 77.10; H 10.94; N 5.65%.

4-(dodecyloxy)aniline (4c)

Rosy solid. Yield: 87%. mp.: 110°C. IR (KBr) cm⁻¹: 3395, 2923, 2850, 1507, 1252. ¹H NMR (CDCl₃, 400 MHz) 6.75 (d, 2H, *J*=8.80 Hz); 6.66 (d, 2H, *J*=8.80 Hz); 3.87 (t, 2H, *J*=6.46 Hz); 1.77 (m, 2H); 1.27 (m, 14H); 0.88 (t, 3H, *J*=13.50 Hz). ¹³C NMR (CDCl₃, 100 MHz) 15.6, 139.3, 116.7, 115.7, 68.7, 31.9, 29.7, 26.1, 22.7, 14.2. Elemental Analyses Calcd. for $C_{18}H_{31}NO$: C 77.92; H 11.26; N 5.05%. Found: C 77.59; H 11.28; N 5.09%.

General procedure for the synthesis of 6a-c

Pyromellitic dianhydride (PMDA) **(5)** (3.08 mmol; 0.672 g) and glacial acetic acid (60 mL) were combined in a three-necked round bottom flask equipped with condenser, and the reaction mixture was stirred under an argon atmosphere for 2 h at 110°C. After the solid had completely dissolved, 4-(octyloxy)aniline **(4a)** (6.78 mmol; 1.50 g) was slowly added to the reaction. The

mixture was stirred and refluxed for 24 h at 100°C. After completion of the reaction, the mixture was cooled to room temperature. Product **6a**, which had precipitated from the reaction mixture, was isolated by filtration, and the residual liquid was extracted with dichloromethane/water (3x20 mL), sodium carbonate solution (20 mL) and dried over anhydrous sodium sulfate. The same procedure was used for the synthesis of compounds **6b** and **6c** using 4-(decyloxy)aniline **(4b)** and 4-(dodecyloxy)aniline **(4c)** as precursors, respectively.

2,6-bis(4-(octyloxy)phenyl)pyrrolo[3,4-f]isoindole-1,3,5,7(2H,6H)-tetraone (6a) Beige solid. Yield: 77%. mp.: 102°C. IR (KBr) cm⁻¹: 3286, 2931, 2846, 1660, 1246. ¹HNMR (CDCl₃, 400 MHz) 7.98 (s, 2H); 7.43 (d, 4H, *J*=8.81 Hz), 6.82 (d, 4H, *J*=9.06 Hz); 3.90 (t, 4H, *J*=13.09 Hz); 1.77 (m, 4H); 1.30 (m, 20H); 0.88 (t, 6H, *J*=6.95 Hz). ¹³C NMR (CDCl₃, 100 MHz) 168.8, 155.9, 130.9, 122.2, 114.9, 68.3, 31.8, 29.3, 26.1, 22.7, 14.1. Elemental Analyses Calcd. for $C_{38}H_{44}N_2O_6$: C 73.05; H 7.10; N 4.48%. Found: C 73.09; H 7.12; N 4.51%.

2,6-bis(4-(decyloxy)phenyl)pyrrolo[3,4-f]isoindole-1,3,5,7(2H,6H)-tetraone **(6b)** Beige solid. Yield: 68%. mp.: 101°C. IR (KBr) cm⁻¹: 3279, 2925, 2846, 1647, 1246. ¹H NMR (CDCl₃, 400 MHz) 7.90 (s, 2H); 7.34 (d, 4H, *J*=8.81 Hz); 6.78 (d, 4H, *J*=8.81 Hz), 3.8 (t, 4H, *J*=13.35 Hz); 1.76 (m, 4H); 1.26 (m, 24H); 0.87 (t, 6H, *J*=13.60 Hz). ¹³C NMR (CDCl₃, 100 MHz) 168.7, 155.9, 130.9, 127.9, 121.9, 114.6, 68.2, 31.9, 29.6, 26.0, 24.1, 22.7, 14.1. Elemental Analyses Calcd. for $C_{42}H_{52}N_2O_6$: C 74.09; H 7.70; N 4.11%. Found: C 74.12; H 7.77; N 4.16%.

2,6-bis(4-(dodecyloxy)phenyl)pyrrolo[3,4-f]isoindole-1,3,5,7(2H,6H)-tetraone (6c)

Beige solid. Yield: 71%. mp.: 99°C. IR (KBr) cm⁻¹:3286, 2919, 2840, 1660, 1246. ¹H NMR (CDCl₃, 400 MHz) 7.69 (s, 2H); 7.35 (d, 4H, *J*=8.81 Hz); 6.82 (d, 4H, *J*=9.06 Hz); 3.90 (t, 4H, *J*=6.55 Hz); 1.75 (m, 4H); 1.26 (m, 36H); 0.88 (t, 6H, *J*=13.60 Hz). ¹³C NMR (CDCl₃, 100 MHz) 168.6, 156.0, 141.2, 130.9, 122.0, 114.7, 68.3, 31.9, 29.7, 29.6, 26.1, 22.7, 14.2. Elemental Analyses Calcd. for $C_{46}H_{60}N_2O_6$: C 74.97; H 8.21; N 3.80%. Found: C 74.99; H 8.23; N 3.84%.

2.3 Theoretical calculations

All the calculations for PDMI molecules presented were computed using the Gaussian16 package [27]. These calculations were performed using a short alkyl chain, for computational efforts economy. A test was made using the same alkyl chain reported in the experimental section and no significant difference was found in the absorption and emission wavelength. For geometry optimizations in the ground and in the first excited state, density functional theory (DFT) was used with the LC- ω HPBE functional, a hybrid functional with exchange-correlation and long-range corrected [28]. The basis set used for geometry optimization was cc-pVDZ. The vertical transitions calculations were performed using Time Dependent Density Functional Theory (TD-DFT) with the jun-cc-pVTZ basis set [29]. This basis set was used because it shows a lower computational cost than an aug-basis set, once the jun- basis set is constructed by reducing diffuse functions from the augmented (aug) basis set [30]. The solvent effects were considered using Polarized Continuum Model (PCM) and the solvents considered were dichloromethane (DMC) and tetrahydrofuran (THF) [31]. The NTO (Natural Transition Orbital) were render using ChemCraft program [32]. Natural transition orbitals dramatically simplify the situation by providing a compact representation of the transition density matrix. This is accomplished using the corresponding orbital transformation of Amos and Hall, which renders the transition density matrix diagonal and provides a unique correspondence between the excited 'particle' and empty 'hole' [33].

3 RESULTS AND DISCUSSION

3.1 Synthesis and spectroscopic characterization

The synthetic methodology for the preparation of all compounds is demonstrated in Scheme 1. The alkylation of 4-hydroxyacetanilide (1) was performed via a Williamson reaction in the presence of K_2CO_3 using three different alkyl bromides with 8, 10 or 12 carbon atoms. The synthesis involved the use of alkoxide ions with an alkyl halide, and the reaction was generally carried out using organic solvents or phase transfer catalysts in the presence of a base followed by reflux for several hours. Compounds **3a-c** were obtained in yields of 91, 88 and 86%, respectively. To obtain the respective amines (**4a-c**)

from **3a-c**, the acetyl group was removed by adding distilled water and concentrated HCl and refluxing the mixture for 24 h. The reaction mixture was then cooled to room temperature and was subsequently basified with NaOH (1 M). The obtained solids were filtered and washed with water to give the desired products in yields of 95, 91 and 87%, respectively.



Scheme 1. Synthetic route for the synthesis of 4a-c.

The PMDI derivatives were prepared by the reaction of two equivalents of the amines (**4a-c**) with pyromellitic dianhydride (**5**) as shown in Scheme 2. The reaction was heated in acetic acid to 110°C for 24 h under an argon atmosphere. The crude product was cooled to room temperature, filtered and the residual liquid was extracted with dichloromethane/water, sodium carbonate solution and dried over anhydrous sodium sulfate to give pure products **6a-c** in 77, 68, and 71% yields, respectively.



Scheme 2. Reaction strategy for the synthesis of 6a-c.

All compounds were characterized by ¹H and ¹³C NMR spectroscopy (Figures SI1-18). For compounds **6a-c**, the obtained NMR spectra in CDCl₃ showed very similar profiles (data not shown). For instance, for compound **6a**, a singlet at

7.98 ppm for the two hydrogens of the pyromellitic system and two 4H doublets with coupling constants of 9.08 Hz centered at approximately 7.38 and 6.79 ppm from the phenyl rings of what used to be the amines can be seen in the aromatic region. Additionally, a 4H triplet located at approximately 4.0 ppm with a coupling constant of 6.44 Hz for the methylene groups adjacent to the oxygen atoms in the alkyl portion of the molecule can be observed. In the 1.77 to 0.86 ppm region, a set of signals for 30 hydrogens can be observed, and these signals correspond to the alkyl moieties of compound **6a**. In the ¹³C NMR spectrum, six different aromatic carbons were found, and the signals at 168.8 and 130.9 ppm from the pyromellitic system were obvious.

3.2 Thermal characterization

The thermal behavior of compounds **6a-c** was investigated using differential thermogravimetric analysis (TGA) (Figure 1). The degradation temperatures were evaluated under an inert N_2 atmosphere. To better visualize the thermal events, the DTG curves (inset) for all the compounds were obtained from the TGA curves.



Figure 1. Thermograms (TGA) and DTG curves of compounds 6a-c.

The overall degradation process of the PMDI derivatives indicates a main degradation event occurs with a mass loss of approximately 80-95% at an initial decomposition temperature higher than 250°C, and the event has a high maximum degradation rate at 350°C. A second thermal event can be observed for all compounds between 400-500°C. The preliminary results indicate that the alkyl chain plays an important role on the thermal behaviors of these compounds, and compound **6c** showed a significantly greater thermal stability with an initial decomposition temperature of approximately 350°C. To better understand the thermal behavior of these derivatives, differential thermal analysis (DTA) was also applied. The presence of an endothermic peak with no loss of mass can be observed for compound **6a** at approximately 100°C due to the fusion of the compounds. The presence of two peaks between 330-474°C related to the decomposition of **6a** can also be observed. The relevant data obtained by DTA are summarized in Table 1. It is worth mentioning that the thermograms of **6b-c** are similar to that of **6a**.

Compound	Molting Point (°C)	T _d (°C) [*]			
Compound		^{1st event}	2 nd event		
6a	102	330	474		
6b	101	320	491		
6c	99	354	480		

Table 1. Differential thermal analysis (DTA) results of compounds **6a-c**, where T_d is the decomposition temperature.

3.3 Electrochemical characterization

The electrochemical properties of compounds **6a-c** were investigated by cyclic voltammetry (CV) (Figure 2). CV is a useful method for measuring electrochemical behavior and evaluating the relative HOMO and LUMO energy levels and the band gap of molecules. The oxidation and reduction processes were directly correlated to electron transfer at the HOMO (ionization potential) and LUMO (electron affinity), respectively.



Figure 2. Cyclic voltammograms of 6a-c in 0.1 TBAPF₆/CH₂Cl₂ at 100 mV s⁻¹.

The reduction process (potential window: 0.0 to -1.8 V vs. Ag/Ag⁺) shows two cathodic waves. The cathodic waves showed two one-electron reduction processes from the pyromellitic diimide group because the molecule can accept one and two electrons to generate the radical anion and a dianion, respectively [34,35]. The oxidation process (potential window: 0.0 to 1.5 V vs. Ag/Ag⁺) exhibits four waves, two anodic and two cathodic, and since the currents show different intensities, the processes can be considered quasi-reversible. These processes correspond to the stepwise formation of radical cations and dications of the compounds [36]. Increasing the length of the flexible alkoxy chains in the evaluated bisimides did not cause a significant change in the energy values of the HOMO and LUMO levels of in the band gap value. To calculate the absolute energies, the redox data were standardized with the ferrocene-ferricenium couple (Table 2). The HOMO energy levels of the bisimides were obtained from the onset potentials of oxidation (Eox) and reduction (Ered) [37]. The electrochemical band gaps (Egel values) of the bisimides were estimated from the difference between the HOMO and LUMO levels. The optical band gaps $(E_g^{opt} \text{ values})$ of **6a-c** were determined by the absorption edge of their solutions. The optical and electrochemical band gaps are summarized in Table 2. The coulombic interaction generally makes the optical band gap smaller than the electrochemical band gap.

Table 2. Electrochemical and optical properties of compounds **6a-c**, where E_{ox} is the onset potential of oxidation, E_{red} is the onset potential of reduction, I_p (HOMO) is the ionization potential, E_a (LUMO) is the electron affinity, E_g is the band gap and λ_{onset} is the absorption onset wavelength.

Parameters	Compounds				
i arameters	6a	6b	6c		
E _{ox} (V vs. NHE) ^a	1.091	1.129	1.060		
E _{red} (V vs. NHE) ^a	-0.751	-0.759	-0.787		
I _p (HOMO) (eV) ^b	-5.531	-5.569	-5.799		
E _a (LUMO) (eV) ^c	-3.689	-3.681	-3.919		
Eg ^{el} (eV) ^d	1.842	1.888	1.847		
λ _{onset} (nm)	740.57	737.55	702.48		
Eg ^{opt} (eV) ^e	1.674	1.681	1.765		

Notes: ${}^{a}E_{ox/red}$ (*vs.* NHE)= $E_{ox/red}$ (*vs.* Ag/Ag⁺) +0.266; ${}^{b}I_{p}$ =-(E_{ox} +4,44) eV; ${}^{c}\lambda_{onset}$: absorption onset wavelength; d Optical band gap calculated from the low energetic edge of the absorption spectrum (E_{g} =1240/ λ_{onset}); ${}^{e}E_{g}$ = E_{a} - I_{p} .

3.4 Photophysical characterization

Figure 3 presents the electronic spectra of PMDI derivatives **6a-c** in tetrahydrofuran and dichloromethane. The relevant data from the UV-Vis absorption spectroscopy are summarized in Table 3. The Strickler-Berg relationship allowed us to calculate the pure radiative lifetimes (τ^0) and the radiative rate constants (k_e^0) [38]. In this relationship, the pure radiative lifetime can be defined as $1/k_e^0$, and the oscillator strength (f_e) can be obtained [39].



Figure 3. UV-Vis absorption (left) and fluorescence emission (right) spectra for **6a-c** in THF ($\sim 10^{-5}$ M). The insets show the photophysical data in dichloromethane ($\sim 10^{-5}$ M).

The PMDI derivatives present absorption maxima in the UV-B region (below 300 nm) due to electronic transitions in the heteroaromatic portion of the molecule. The molar absorptivity coefficient (ϵ) for each of the absorption maxima and the calculated radiative rate constants (k_e^0 values) indicate that the spin- and symmetry-allowed electronic transitions were related to the ${}^{1}\pi\pi^{*}$ transitions. Despite the observed allowed electronic transitions, low values of the oscillator strength could be calculated. Notably, in both solvents, these compounds each presented a very intense absorption band below 270 nm, probably related to the benzenoid ring present in the structure. This assumption was corroborated by the lack of emission observed using 250 nm as the excitation wavelength. Changes in the alkyl chain length did not seem to affect the photophysical behavior of these compounds in the ground state. In addition, the absence of solvatochromism revealed that these compounds, despite the presence of donor and acceptor moieties in their structure, do not present ICT character in the ground state. The similar radiative lifetime values (τ^{0}) indicate that after radiation absorption, the fluorophores populate the same excited state.

The fluorescence emission spectra of the PMDI derivatives in both solvents are also shown in Figure 3. The emission curves were obtained by exciting the compounds at their maximum absorption wavelengths. The relevant data from the fluorescence emission spectra are listed in Table 3. These compounds present very similar photophysical behaviors in THF, and a main fluorescence emission located at 326 nm could be observed for all compounds, indicating that in this solvent, the changes in the chemical structure of the fluorophores do not have a substantial impact on the location of the fluorescence maxima. Moreover, the lack of solvatochromism in the emission curves shows that no charge-transfer occurs in the excited state. On the other hand, in the more polar solvent, dichloromethane, the emission curves of 6a and 6b are quite different from their curves in THF. Compound 6a, which has the smaller alkyl chain, presents a locally excited emission band at 326 nm and an additional redshifted band located at 400 nm probably due to ICT character. In addition, compound **6b** presents a broader emission band that what was seen in THF, which may indicate an ICT mechanism, is active for this fluorophore. The low solubility of these compounds prevented additional investigations in more polar solvents or even fluorimetric titrations. In spite of the significant rigidity of the PMDI core, low values were found for the fluorescence quantum yields (0.019-0.069). In this case, based on the free bond rotation of the benzene ring, as well as the presence of the alkoxy chains, different types of non-radiative processes could be envisaged, such as internal conversion and vibrational relaxation [40-43], which may contribute significantly to the electronic deexcitation, where the molecule loses its acquired excess energy.

Table 3. Relevant photophysical data of the UV-Vis spectra of **6a-c**, where λ_{abs} is the absorption maxima (nm), ε is the molar absorptivity (x10³ L mol⁻¹ cm⁻¹), f_e is the calculated oscillator strength, k_e^0 (x10⁸) is the calculated radiative rate constant (s⁻¹), τ^0 is the inherent emission lifetime (ns), λ_{em} is the emission maxima (nm), $\Delta\lambda_{ST}$ is the Stokes shift (cm⁻¹), and Φ_{FL} is the fluorescence quantum yield.

	Solvent	λ_{abs}	λ_{em}	ε	f _e	k ⁰ e	τ0	Eg ^{opt}	Δλ _{ST}	Φ_{FL}
62	Dichloromethane	284	328	8.72	0.12	1.49	6.72	4.38	4723	0.019
Ua	Tetrahydrofuran	290	312	8.04	0.12	1.41	7.10	4.27	2431	0.044
Gh	Dichloromethane	284	328	6.26	0.09	1.08	9.26	4.38	4723	0.035
ao	Tetrahydrofuran	290	312	5.96	0.09	1.07	9.33	4.27	2431	0.069
60	Dichloromethane	284	328	7.25	0.10	1.24	8.04	4.38	4723	0.032
00	Tetrahydrofuran	290	312	7.17	0.10	1.21	8.26	4.27	2431	0.050

3.5 Theoretical calculations

The calculated geometry for the ground and first excited states of the PMDI's in DCM and THF are summarized in Table 4. The molecules in both solvents presented small geometry differences, mostly in the dihedral angle between carbonyl carbon, nitrogen and the two carbons of benzene. This difference is expected, since the ground state geometry is not planar.

Table 4. Minimum energy structures of the ground state (S_0) and the first excited state (S_1) for the PDMI generic structure, obtained from the LC- ω HPBE/cc-pVDZ calculations in DCM and THF.



 ϕ is the dihedral angle between selected atoms.

The Table 5 presents the Natural Transition Orbitals (NTOs) for S0 and S1. It is possible to see that these orbitals are π , so we assume that a $\pi \rightarrow \pi$ * transition is occurring. The molecular orbitals do not show a spatial separation in the S0 \rightarrow S1 transition, therefore, we do not observe a charge transfer, but only local excitations.



Table 5. NTO of PDMI in the ground (S_0) and first excited states (S_1) in DCM and THF. The calculations were performed with LC- ω HPBE/cc-pVDZ level.

Analyzing the Table 6, we can see that the calculated absorptions wavelengths are very close to the experimental ones, mainly in the THF, where the difference between the theoretical and the experimental results were only 5 nm. The obtained values for emission wavelengths were not so close using the LC- ω HPBE functional, since the difference between the calculated and experimental values were around 100 nm. It was experimentally observed that the absorption wavelengths in DCM were smaller than in THF, and this was observed in the calculations.

Table 6. Photophysical data obtained from the LC- ω HPBE/jun-cc-pVTZ calculation in DCM and THF for PDMI, where λ_{abs} is the absorption wavelength (nm), λ_{emis} is the emission wavelength (nm), μ_{S0} is the dipole moment (Debye) for the ground state, μ_{S1} is the dipole moment (Debye) for the first excited state, f_{abs} is the absorption oscillator strength and f_{emis} is the emission oscillator strength.

Solvent λ _{abs}	µ _{so}	$oldsymbol{f}_{abs}$	λ_{em}	μ _{s1}	$m{f}_{em}$
DCM 293.66	1.8029	0.0022	451.79	12.1934	0.0056
THF 294.66	1.8388	0.0025	451.77	12.1922	0.0056

4. Conclusions

A series of new pyromellitic diimide (PMDI) derivatives was synthesized and characterized. The photophysical investigations showed that all compounds presented absorption in the UV-B region (~290 nm). The band-gaps were

calculated from the onset peak values to be approximately 4.03 eV. The compounds are photoactive in the UV-A region (312-328 nm) with a small solvatochromic effect in the excited state ($\Delta\lambda_{em}$ =16 nm). The thermal properties were measured, and all the synthesized compounds showed high thermal stability. Spectroelectrochemical measurements showed two waves due to the formation of the radical anion and a dianion. Theoretical calculations showed the coefficients for the fundamental state and first excited state appeared to be π -type orbital. Thus, it was assumed that transitions of type $\pi \rightarrow \pi^*$ were taking place.

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23

- New pyromellitic diimide (PMDI) derivatives presenting alkyl chains with different sizes.
- ✓ The compounds showed high thermal stability (Td > 300° C).
- ✓ The electrochemical reduction showed the formation of the radical anion and a dianion.
- ✓ The electrochemical oxidation showed formation of radical cations and dications.
- ✓ Transitions type $\pi \rightarrow \pi^*$.

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