New porphyrins tailored as biodiesel fluorescent markers

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ABSTRACT

This work reports the synthesis, characterization, and evaluation of new porphyrins tailored to become biodiesel fluorescent markers. The compounds were obtained by the synthetic modification of the commercially available porphyrin 5,10,15,20-meso-*tetrakis*(pentafluorophenyl)porphyrin ($TPPF_{20}$) using ethanol and hexadecan-1-ol (cetylic alcohol) as nucleophilic reagents.

The stability of the marked biodiesel fuel solutions was investigated every 15 days for a total period of 3 months, and under different storage temperature and light exposure condition, simulating the conventional stock conditions. The influence of the different substituents of the porphyrins on the fluorescence properties of the biodiesel fuel markers was also assessed.

The resulting porphyrins were highly soluble in biodiesel fuel and displayed strong fluorescence characterized by two strong emission bands. The fluorescent markers did not affect the biodiesel physical properties and were stable in storage conditions for at least 3 months at a concentration of 4 ppm.

The best storage condition was found to be absence of light and 6 °C; the limit of detection by photoluminescence technique had magnitude of 10^{-13} mol L^{-1}.

The synthesized porphyrins were characterized by nuclear magnetic resonance (^{1}H-NMR and ^{19}F-NMR), mass spectrometry (HRMS), ultraviolet visible absorption spectroscopy, and photoluminescence spectroscopy.

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1. Introduction

It is well known that the fuel industry is one of the most important and profitable commercial areas. Fuel production, distribution, and taxation policies are the exclusive responsibility of each country or government. The fuel rating process itself relies on the characteristics of each fuel, especially those regarding its uses and applicability. In this context, the fact that the same fuel can be used for different purposes is taken into account, thereby leading to distinct taxations [1].

Unfortunately over the years the fraudulent adulteration of fuels has been rising, which means that their indiscriminate misuse is growing fast due to a mixture of low quality products with premium-quality ones. Even solvents that serve a different kind of application are being added to fuels, to guarantee low prices on a daily basis. Hence, it is mandatory that new policies are developed in order to fight against this kind of practice. Fuel tagging or marking, appears to be one of the most important measures in this sense, because it allows

for fuel quantification and identification, their origin along with production chain. Therefore, this method is a potential procedure for discouraging this kind of misuse or making it at least traceable.

Friswell described once that a marker is a substance that can be dissolved in a liquid and later be detected in such liquid by performance of a chemical or physical test on the tagged (marked) liquid. They are necessary for a clear distinction between chemically or physically similar liquids [2].

The fuel marking systems employed in past decades frequently used organic pigments [3]. Several substances have been used to tag petroleum fuel and derivatives, but they all possess negative characteristics such as poor solubility in hydrophobic environment or low stability under storage conditions. Historically, various other problems have accompanied the use of dyes as fuel markers, including crystallization [4] upon standing or storage.

A few years ago some coumarin derivatives [2], naphthalocyanines [4], and phthalocyanines were tested as fluorescent markers for petroleum fuel derivatives because of their fluorescent properties and stability. Besides, these compounds are invisible under the naked eye and visible light, but they can be easily detected by UV light since they offer higher sensitivity compared to the commonly used organic dyes.

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Hence, some desirable characteristics of fluorescent markers include:

1) Good solubility in the fuel to be marked;
2) High fluorescence intensity in regions distinct from those where fluorescent components in the marked fuels emit, which should enable their use at low concentrations;
3) Invisibility under ambient light;
4) Stability over the marked fuel storage life (minimum of one month);
5) Easy detection by a simple test;
6) Possibility of scalable syntheses at fair prices [2,5].

Recently, Puangmalee and collaborators have synthesized a new fluorescent porphyrin derived from cardanol for use as a petroleum diesel fluorescent marker [5]. Indeed, porphyrins appear as a great alternative for fuel labeling due to their intrinsic photophysical characteristics, which make them very attractive as photosensitizing compounds. In addition, these macrocycles possess synthetic tractability and good stability under the right storage conditions. The meso-tetra substituted porphyrins, in particular, can be simply prepared by acid-catalyzed pyrrole–aldehyde condensations, followed by the porphyrinogen intermediate oxidation at ambient temperature and atmospheric pressure, in good yields [6,7]. Furthermore, nucleophilic substitution reactions of the four *para*-fluoro groups on TPPF$_{20}$ have been extensively studied. The reactivity of the *para*-fluoro group on the pentafluorophenyl moiety varies significantly depending on the specific primary nucleophile that is employed. The reactivity increases ongoing from harder to softer nucleophiles: HO–CH$_2$R << H$_2$N–CH$_2$R < HS–CH$_2$R [8].

In order to achieve all the above mentioned desired characteristics for a good fuel labeling system, the synthesis, characterization, and evaluation of new porphyrins derived from TPPF$_{20}$ was accomplished, with a view to obtaining "*invisible*" fluorescent biodiesel markers. Biodiesel is commonly defined as a mixture of fatty acids alkyl esters produced mainly by transesterification reaction between vegetable oils or fats and an alcohol such as methanol or ethanol in the presence of a catalyst, usually NaOH, in anhydrous conditions, which also produces glycerol as a byproduct. Biodiesel has recently been classified as a substitute of petroleum diesel mostly because the two fuels share similar physical and chemical properties [9]. Moreover, biodiesel is a renewable fuel and is made from nontoxic, biodegradable resources [10].

In this work, the synthesis of the target compounds was attempted by modification of the commercially available porphyrin 5,10,15,20-meso-*tetrakis*(pentafluorophenyl)porphyrin (TPPF$_{20}$) using ethanol and hexadecan-1-ol (cetylic alcohol, Fig. 1).

Studies on a spectrofluorometric detection method for the markers and investigation of the stability of the marked biodiesel fuel in four different storage conditions were also carried out. In addition, the marked and unmarked biodiesel fuel physical properties were tested, in order to evaluate the applicability of the synthesized porphyrins as biodiesel markers.

2. Material and methods

2.1. Reagents and measurements

All reagents were of analytical grade. Tetrahydrofuran (THF) was purchased from Tedia® (Engenho Novo, RJ, BRAZIL) and ethanol was acquired from Synth® (Diadema, SP, BRAZIL); both solvents were used after purification according to standard procedures [11,12]. TPPF$_{20}$ was supplied by Mid-Century® (Chicago, IL, USA). Hexadecan-1-ol was obtained from Synth® (Diadema, SP, BRAZIL) and used without further purification.

1
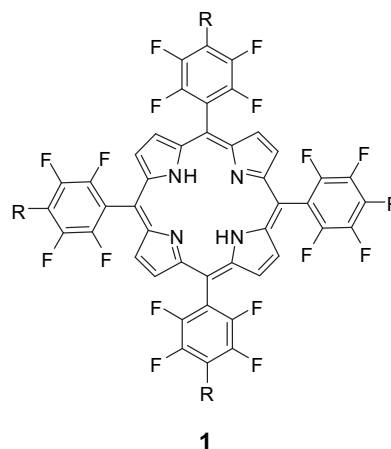
Marker	R
2	HO⌒⌒⌒⌒⌒⌒⌒⌒
3	HO⌒

Fig. 1. TPPF$_{20}$ structure.

^{1}H-NMR and ^{19}F-NMR spectra were acquired on a Brüker AVANCE 500 and on Brüker AVANCE 300 spectrometers operating at 500.13 MHz and 300.13 MHz, respectively. Measurements were carried out at ~300 K. Deuterated chloroform (CDCl$_3$) was used as a solvent and tetramethylsilane (TMS) was employed as an internal reference. The chemical shifts are expressed in δ (ppm) and the coupling constants (J) are given in hertz (Hz).

The high-resolution ESI-MS analyses were performed on an UltroTOF-Q (Bruker Daltonics, USA) fitted with an electrospray ionization (ESI) source operating in the positive ion mode.

The UV–vis absorption spectra were recorded on an HP Diode Array 8453A spectrophotometer using biodiesel as primary solvent.

The porphyrins' emission and excitation spectra in solution were obtained at ~300 K, using a HORIBA® – SPEX Triax 550 Fluorolog 3 Spectrofluorometer (CCD array – Synapse). The recorded spectra were corrected for lamp intensity by using the apparatus software.

Liquid chromatography was carried out by using silica gel 70–230 mesh, and the preparative thin layer chromatography (TLC) was conducted on 20 × 20 cm Aluminium sheets (1 mm thick) – Merck TLC Silica gel 60 F$_{254}$.

2.2. Synthesis of the meso-tetrakis(2,3,5,6-tetrafluoro-4-(hexadecyloxy)phenyl)porphyrin (**2**)

TPPF$_{20}$ (**1**) (50 mg/0.051 mmol) was added into a two-neck round flask. Then, 149 mg (0.616 mmol) of hexadecan-1-ol, 288 mg (5.1 mmol) of KOH and 20.0 mL of THF solvent were subsequently added, and the reaction mixture was stirred for 4 h under reflux (~70 °C) and inert atmosphere (Argon). The reaction products were extracted with diethyl ether (3 × 10.0 mL) and washed with saturated NaHCO$_3$ solution. The organic fractions were dried under MgSO$_4$, and the solvent was distilled off under vacuum. Product **2** was purified by column chromatography in silica gel using n-hexane/toluene (85:15) as eluent. Porphyrin **2** was obtained in 98% yield.

2.2.1. Data for porphyrin 2
^{1}**H-NMR** (CDCl$_3$, 500.13 MHz): δ (ppm): −2.89 (*s*, 2H); 0.87 (*t*, J = 6.7 Hz, 12H); 1.30 (*m*, 96H); 1.49 (*q*, J = 7.6 Hz, 8H); 1.65 (*q*, J = 7.4 Hz, 8H); 2.02 (*q*, J = 7.4 Hz, 8H); 4.59 (*t*, J = 6.7 Hz, 8H);
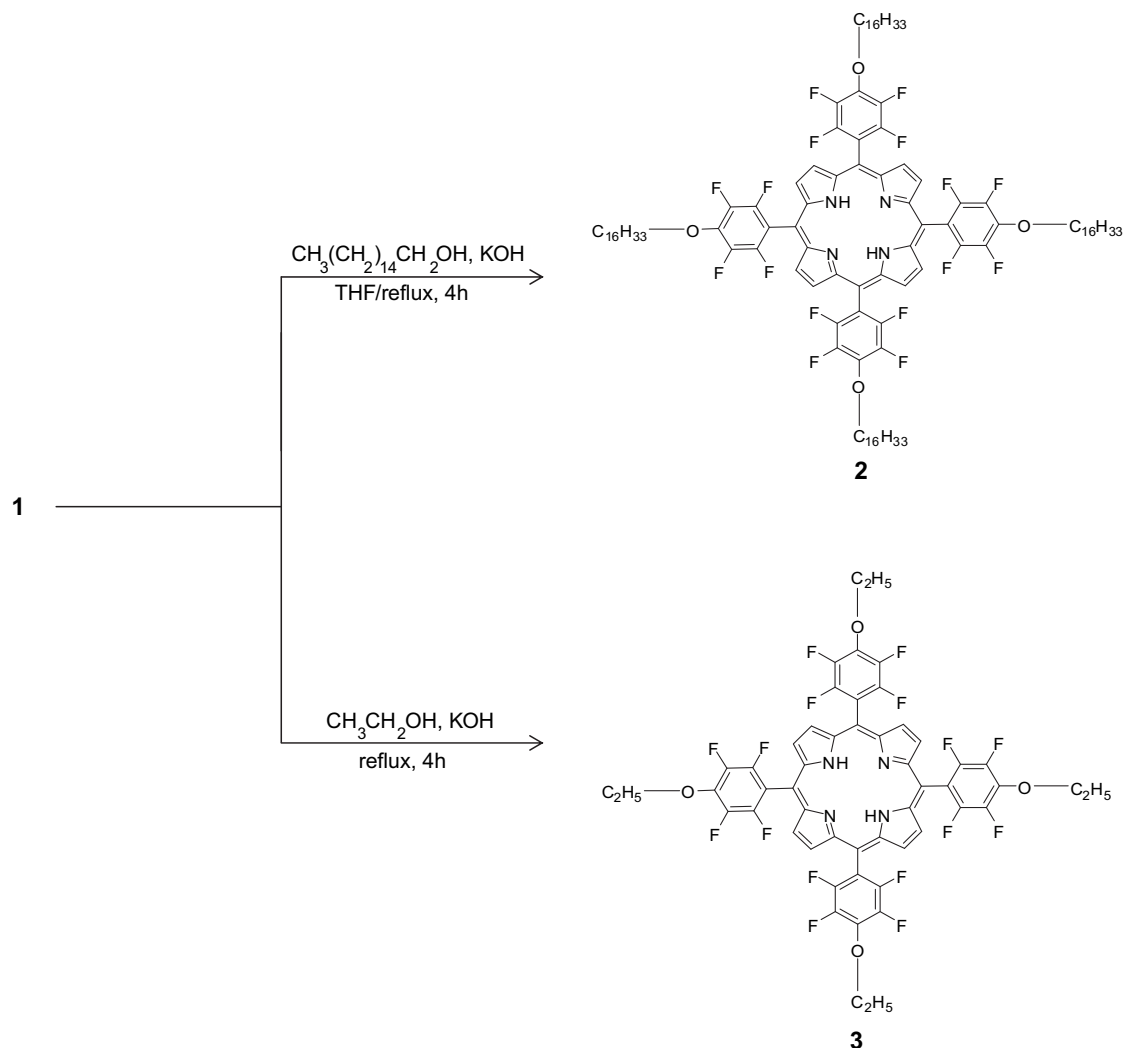
Scheme 1.

and 8.92 (*s*, 8H). ^{19}**F-NMR** (CDCl$_3$, 300.13 MHz): δ (ppm) -138.9 (dd, 8F) and -157.3 (dd, 8F) [13]. **HR–ESI–TOF-MS**: theoretical, [**M** + 2H]$^{2+}$, m/z = 933.0483, found, [**M** + 2H]$^{2+}$, m/z = 933.0512 (Δ = 3.1 ppm).

2.3. Synthesis of the meso-tetrakis(2,3,5,6-tetrafluoro-4-(ethoxy) phenyl)porphyrin (**3**)

TPPF$_{20}$ (**1**) (50 mg/0.051 mmol) was added to a two-neck round flask. Then, 144 mg (2.55 mmol) of KOH and 10.0 mL of ethanol were subsequently added, and the reaction mixture was stirred for 4 h under reflux ($\sim$80 °C) and inert atmosphere (Argon). The reaction products were extracted with diethyl ether (3 × 10.0 mL) and washed with saturated NaHCO$_3$ solution. The organic fractions were dried under MgSO$_4$, and the solvent was distilled off under vacuum. Product **3** was purified by column chromatography in silica gel using toluene as single eluent. Porphyrin **3** was obtained in 95% yield.

2.3.1. Data for porphyrin **3**
^{1}**H-NMR** (CDCl$_3$, 500.13 MHz): δ (ppm): -2.89 (*s*, 2H); 1.67 (*t, J* = 7.0 Hz, 12H); 4.68 (*q, J* = 7.0 Hz, 8H); and 8.92 (*s*, 8H). ^{19}**F-NMR** (CDCl$_3$, 300.13 MHz): δ (ppm) -138.2 (dd, 8F) and -156.7 (dd, 8F)

[11]. **HR-ESI-TOF-MS:** theoretical, [**M** + H]$^+$, m/z = 1079.2090, found, [**M** + H]$^+$, m/z = 1079.2109 (Δ = 1.8 ppm).

2.4. Biodiesel synthesis by transesterification

The biodiesel fuel used in this work was synthesized as described in the literature by Figueira et al, following the classic transesterification route [14].

2.5. Effects of porphyrins 2 and 3 on the biodiesel fuel physical properties

The influence of porphyrins **2** and **3** on the physical properties of biodiesel samples was evaluated. To this end, a stock solution of each marker with a concentration of 100 ppm was prepared by dissolving 10 mg of markers **2** or **3** in the biodiesel fuel and filling up a volumetric flask up to 100 mL. These solutions were diluted 25 times with biodiesel fuel, to obtain a 4 ppm solution of the marked biodiesel. The free biodiesel samples (unmarked fuel) and the marked biodiesel samples were submitted to tests according to the ASTM and CEN methods [15,16].

2.6. Stability test for the fluorescent markers 2 and 3 in the biodiesel fuel

The storage stability test was performed by tagging four biodiesel fuel samples with markers 2 or 3 at a concentration of 4 ppm. Subsequently, the samples were submitted to four different storage conditions, bearing in mind that the porphyrin macrocycles are photosensitive and can be degraded by exposure to light and high temperature. The 4 ppm-marked biodiesel solutions were prepared by diluting 1 mL of the 100 ppm stock solution with biodiesel in eight different 25 mL volumetric flasks, four flasks for each marker 2 or 3.

The exposed solutions had their fluorescence emission spectra measured every 15 days, for a total period of 90 days (λ_{exc} = 414 nm).

2.7. Linear working range for porphyrins 2 and 3

Linear Working Range is the range where the results are proportional to the analyte concentration present in the sample (calibration curve). In our case this corresponded to porphyrins 2 and 3 concentrations presenting minimum and maximum detection with reliable results. In order to obtain the calibration curve, several solutions of markers 2 or 3 with distinct concentrations were prepared in biodiesel fuel, and their fluorescence emission spectra were measured (λ_{exc} = 414 nm).

2.8. Limit of detection for porphyrins 2 and 3

Limit of detection is the minimum concentration at which the analyte can be identified by the selected technique. In this way, porphyrins 2 and 3 were identified by their characteristic emission band with maximum at 710 nm. The limit concentration was found to be of the order of magnitude of 10^{-13} mol L^{-1} in both cases. The referred measurements were accomplished with a Hellma® triangular quartz cell (111-QS Quatrz Suprasil®) λ_{exc} = 414 nm (Soret band).

2.9. Limit of quantitation/sensitivity for porphyrins 2 and 3

Limit of Quantitation/Sensitivity is the minimum analyte concentration that can be quantified with an acceptable level of precision and accuracy under the tested conditions. In the case of a calibration curve, the sensitivity is given by its slope. The sensitivity in this case was found to be 0.2 ppm for both porphyrins.

2.10. Quantitative measurements of porphyrins 2 and 3 in biodiesel

In order to obtain a calibration curve, a series of solutions of markers 2 and 3 were prepared at different concentrations, namely 0.2; 0.4; 0.6; 0.8; 1.0; 2.0; and 4.0 ppm, by respectively pipetting 0.5; 1.0; 1.5; 2.0; 2.5; 5.0; and 10.0 mL from the 20 ppm stock solution into 50 mL volumetric flasks, which were then filled up with biodiesel. The fluorescence emission spectra were recorded on a spectrofluorometer (λ_{exc} = 414 nm/Soret band), and the calibration curves of each marker were achieved by plotting the emission intensity at 710 nm versus concentration in ppm. The resulting equations extracted from the curves were used to quantify markers 2 and 3 in the biodiesel samples.

3. Results and discussion

3.1. Synthesis of the fluorescent markers 2 and 3

The synthesis of the novel tetra-functionalized (penta-fluorophenyl)porphyrins 2 and 3 was accomplished by means of the highly selective nucleophilic substitution of the four para-fluoro atoms in the 5,10,15,20-meso-tetrakis-(pentafluorophenyl) porphyrin (1) using an improvement to a described procedure [17]. The products were obtained in high yields (98 and 95%, respectively) by using hexadecan-1-ol, in THF, or ethanol as nucleophiles under reflux, as shown in Scheme 1.

Porphyrins 2 and 3 were largely soluble in nonpolar environments such as dichloromethane, n-hexane, and biodiesel. They are very soluble in ethanol, as well. They both display the characteristic Soret band (414 nm) with experimental molar extinction coefficients, ε, of 2.67×10^5 L mol^{-1} cm^{-1} and 2.91×10^5 L mol^{-1} cm^{-1}, respectively, and four Q bands (507, 538, 585, 657 nm) in biodiesel solutions, as shown in Fig. 2a,b.

The spectra presented in Fig. 2a,b are in agreement with the typical electronic absorption spectra of porphyrins, and they follow the four-orbital model described by Martin Gouterman and reinforced by Simpson and Platt [18–22]. The spectra consist of a strong transition to the second excited state at about 414 nm (Soret band or B band) and four weak transitions to the first excited state from 500 to 660 nm (Q bands). In order to better visualize the four Q bands, solutions of markers 2 and 3 were prepared at a higher concentration than the initial one. The insets of Fig. 2 a,b show the Q bands for porphyrins 2 and 3, respectively.
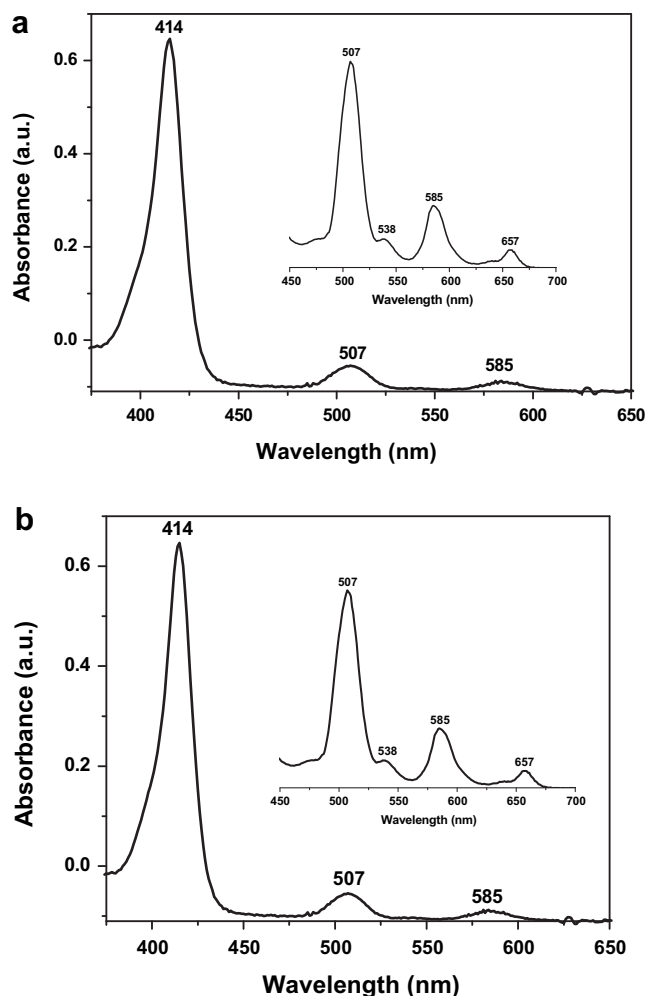

Fig. 2. UV–visible absorption spectra of the synthesized porphyrins: a) 2 and b) 3.

Table 1
Physical properties of the unmarked and marked biodiesel samples.

Physical characteristics	Method[a,b]	Biodiesel[c]		
		Unmarked	Marked/(2)	Marked/(3)
Aspect/Color	Visual	CFI[d]	CFI[d]	CFI[d]
Specific gravity at 20 °C (kg/m³)	D 4052	882	881	881
Kinematic viscosity at 40 °C (mm²/s)	D 445	5.12	5.19	5.19
Flash Point (°C)	D 93	176.0	176.0	176.0
Cetane index	D 613	58.0	59.0	59.0
Sulfur content (mg/kg)	EN 20884	39.0	39.0	39.0

[a] American Society for Testing Materials (ASTM);
[b] European Committee for Standardization (CEN);
[c] Biodiesel samples marked with markers **2** and **3** at 4 ppm;
[d] Clear and free of impurities;

3.2. Spectrofluorometric method for the quantitative determination of fluorescent markers *2* and *3* in biodiesel

The characteristic fluorescence of the macrocycles was used to quantify markers **2** and **3** in the biodiesel samples. First of all, seven samples with concentrations of 0.2; 0.4; 0.6; 0.8; 1.0; 2.0; and 4.0 ppm were prepared by diluting a stock solution of the markers **2** or **3**, 20 ppm, previously prepared in biodiesel fuel. Then, the emission intensities of the porphyrins in the samples were measured in order to construct a calibration curve.

The standard calibration equation was found to be $Y = 5.2 \times 10^3 X$ with a correlation coefficient equal to 0.9929 for porphyrin **2**, and $Y = 5.1 \times 10^3 X$ with a correlation coefficient equal to 0.9912 for porphyrin **3**. The equations generated by the curves were used as a parameter to measure the quantity of fluorescent marker in biodiesel solutions.

3.3. Storage stability test for the fluorescent markers *2* and *3* in biodiesel fuel

Usually biodiesel is stored for up to three months before being released for market consumption. Therefore, eight marked biodiesel samples, four of each marker (**2** and **3**) were prepared, and exposed to four different storage conditions, for 90 days:

a) At room temperature (22 °C) and under ambient light;
b) At room temperature (22 °C) and in the absence of light;
c) At refrigerator temperature (6 °C) and in the absence of light;
d) At furnace temperature (45 °C) and in the absence of light.

Afterwards, their fluorescence emission spectra, characterized by two intense bands (maxima at 642 nm and 710 nm/ $\lambda_{exc} = 414$ nm), were measured every fifteen days (15, 30, 45, 60, 75, and 90 days) for a total period of three months (90 days). On the basis of the relative intensity of the band at 710 nm detected for both porphyrins, it is possible to state that markers **2** and **3** were stable to the storage and can be reliably used as biodiesel markers. In addition, the different peripheral substituents on the porphyrin ring cause minor changes to the absorption features and there is minimal difference in the emission behavior of both porphyrins. Moreover, the best storage condition was found to be 6 °C and absence of light, as expected. The graphics and results can be seen in the Supplementary data.

3.4. Influence of the fluorescent markers *2* and *3* on the physical properties of the biodiesel fuel

An investigation of the influence of markers **2** and **3** on the physical properties of the biodiesel fuel was accomplished, to ensure that the labeling procedure would not affect the use of the fuel.

The American Society for Testing and Materials (ASTM) and the European Committee for Standardization (CEN) methods were chosen to carry out tests on samples of marked and unmarked biodiesel fuel [13,14]. The results are summarized in Table 1.

The results in Table 1 show that markers **2** and **3** did not significantly affect the physical properties of the biodiesel fuel once the marked and unmarked samples exhibited similar properties.

4. Conclusions

In the present work, two tetra-substituted meso-*tetrakis* (pentafluorophenyl)porphyrins containing 1-hexadecyloxy- and ethoxy-substituents in the four *para*-fluoro positions of the TPPF$_{20}$ macrocycles were successfully synthesized, rendering two markers soluble in both hydrophobic and hydrophilic environments such as biodiesel and ethanol. Moreover, it was confirmed that the different peripheral substituents on the porphyrin ring only caused minor changes to TPPF$_{20}$ absorption features.

The new porphyrins exhibited suitable spectrophotometric behavior. Their fluorescence was characterized by two strong emission bands centered at 642 nm and 710 nm ($\lambda_{exc} = 414$ nm). These characteristics aided their quantification in biodiesel solutions, performance of a storage stability test in which the best storage condition was found to be 6 °C and absence of light, as expected. A study of their behavior regarding their physical and chemical properties was also carried out. The obtained results attested that these porphyrins are potential fluorescent markers for biodiesel fuel.

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.dyepig.2011.05.020.

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