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Dedicated to Professor Alexandru T. Balaban on the occasion of his 85th anniversary

A NEW PHENOTHIAZINE BLUE LIGHT EMITTER. SYNTHESIS, STRUCTURE AND PHOTOPHYSICAL PROPERTIES

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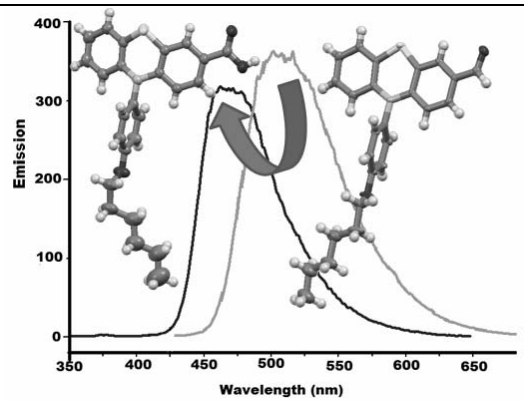
The paper presents the obtaining of a phenothiazine based blue light emitter *via* an efficient oxidation process of a phenothiazine based aldehyde to the corresponding carboxylic acid in basic media – a quite unusual synthetic route, evidenced in the approach of Horner–Wadsworth–Emmons coupling reaction. The structure of the reagent and corresponding product was evidenced by spectroscopic methods as Fourier transformed infrared spectroscopy and nuclear magnetic resonance spectroscopy, while unequivocal proof of the reaction was brought by single crystal X-ray diffraction. The introducing of the carboxyl unit on the phenothiazine core proved to be a good pathway to obtain blue light emission.



INTRODUCTION

Phenothiazine is a heterocyclic fused ring, intensely studied as a component of materials addressed for electronic or opto-electronic devices as photovoltaic cells, field effect transistors, light emitting diodes or chemical sensors.[1-4] The phenothiazine ring contains rich electron sulfur and nitrogen atoms which confer a strong electron-donating character, much more intense as compared to the compounds containing only one heteroatom[5], which recommends it as building block of highly electron delocalized donor-acceptor dyes. On the other hand, phenothiazine has an excellent thermal and electrochemical stability, essential features in high performance applications. In this context, an intense activity is directed to the synthesis of new phenothiazine derivatives.[6-10] The introduction of carboxylic acid functionality on the phenothiazine ring is of interest not only for the obtaining of new chromophoric compounds, but also of intermediates in further reactions.

The oxidation reaction is a fundamental chemical transformation widespread in organic chemistry,

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especially for industrial purposes. The use of oxidation reaction to transform aldehydes to the corresponding carboxylic acids is of long standing interest for synthetic organic chemistry, due to the use of carboxylic acids in biological and large applicative areas.[11-13] Usually, the oxidation proceeds in the presence of stoichiometric amounts of toxic or expensive oxidants such as potassium permanganate, chromium VI reagents, chlorides or peroxides often associated with harmful organic solvents such as benzene, formic acid, methylene chloride, etc. For these reasons, an important attention goes to the developing of new oxidation procedures to effect old reaction in a more eco-friendly manner.

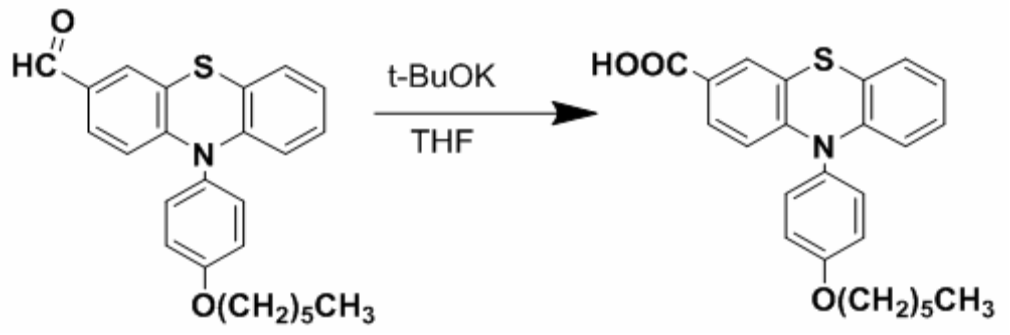
In this paper we report the conversion of an aldehyde functionalized phenothiazine into the corresponding carboxylic acid derivative in mild reaction conditions, in the presence of tBuOK – a synthetic route never reported in the literature up to now.

RESULTS AND DISCUSSION

The phenothiazine based carboxylic acid named 10-(4-hexyloxyphenyl)-10H-phenothiazine-3-carboxylic (**2Ac**) acid has been obtained from 10-(4-hexyloxyphenyl)-10H-phenothiazine-3-carbaldehyde (**1A**), as the main product during a Horner-Wadsworth-Emmons coupling reaction – known to be of interest especially for the preparation of alkenes from aldehydes. Compared to the standard procedure[14], the reaction was performed in the absence of an inert atmosphere, this appearing to drastically influence the reaction pathway leading to a carboxylic functionality instead a double bond, the oxidation of the formyl unit being the main reaction. The synthetic pathway is represented in Scheme 1.

The unexpected synthetic pathway was demonstrated by spectroscopic and X-ray diffraction analysis. As can be seen in Fig. 1, a comparison of the **FTIR spectra** of the aldehyde reagent and of the carboxylic acid product shows that the absorption band at 1670 cm^{-1}, specific to the vibration of the C=O group into aldehyde unit is shifted to a higher wavenumber at 1730 cm^{-1}, indicating its transformation into a carboxylic unit.[15] Besides, the absorption band characteristic to the O-H stretch can be observed as a broad peak around 3450 cm^{-1}, which could also be the signature of inter-molecular H-bonds[16] and H-bonding with water, characteristic to the carboxylic compounds.[17] All the other bands belonging to the aliphatic or aromatic units[18,19] are present in the both spectra, as detailed in the Experimental part.

Comparing the **NMR spectra** it can be observed that the clear chemical shift at 9.7 ppm – belonging to the aldehyde proton in the **1A** spectrum (Fig. 2a) – completely disappears in the NMR spectrum of the corresponding carboxylic acid (**2Ac**), while a new broad peak appears around 12.6 ppm. This last band is characteristic to the proton into the carboxylic unit which can easily hydrogen-deuterium exchange with the solvent (Fig. 2b).[20] All other aromatic and aliphatic protons were found with similar chemical shift values (see Experimental part), in the right integral ratio, indicating that only the aldehyde group transforms into carboxylic moiety, the rest of the molecule keeping its integrity during the oxidation process. Small differences are observed for the chemical shift of the protons neighbor to the sulfur heteroatom, this reflecting the different withdrawing effect of carboxyl *versus* carbonyl groups (Fig. 2c,d). Thus, their doublets are shifted from 6.31 ppm (J=8Hz) to 6.155 ppm (J=12Hz), and from 6.23 ppm (J=8Hz) to 6.12 ppm (J=8Hz), respectively.



Scheme 1 – Synthesis of the 10-(4-hexyloxyphenyl)-10H-phenothiazine-3-carboxylic acid.

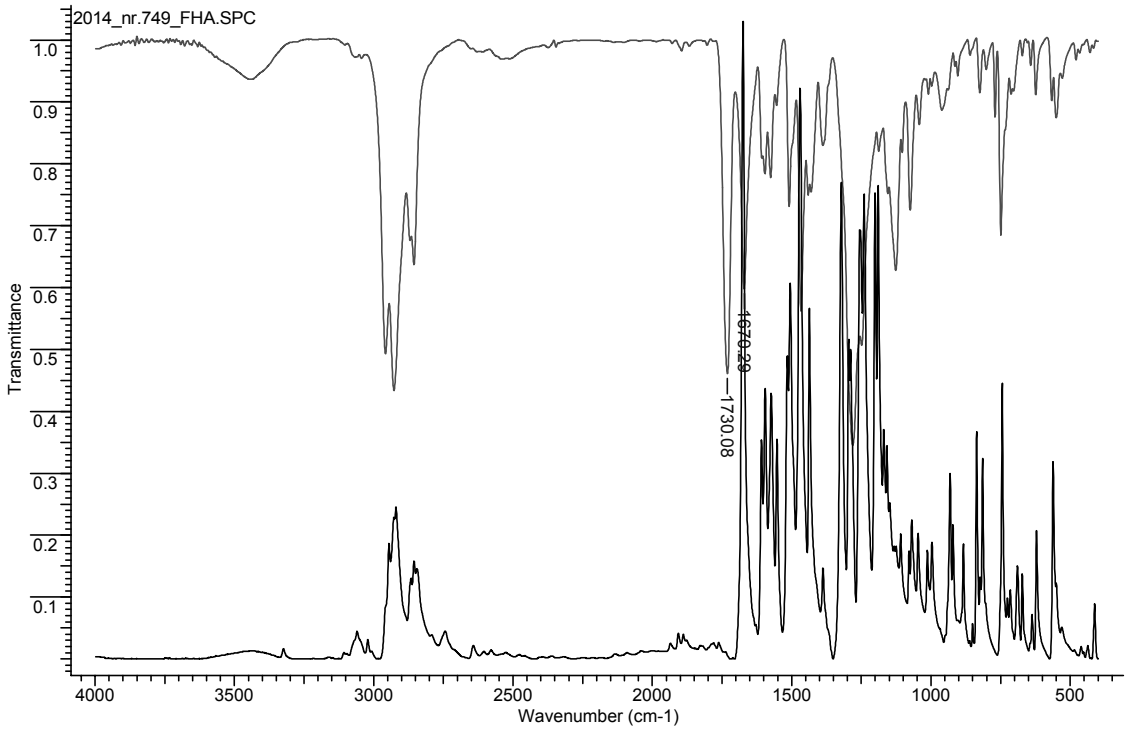


Fig. 1 – FTIR spectra of phenothiazine aldehyde (black) and of the corresponding carboxylic acid (red).

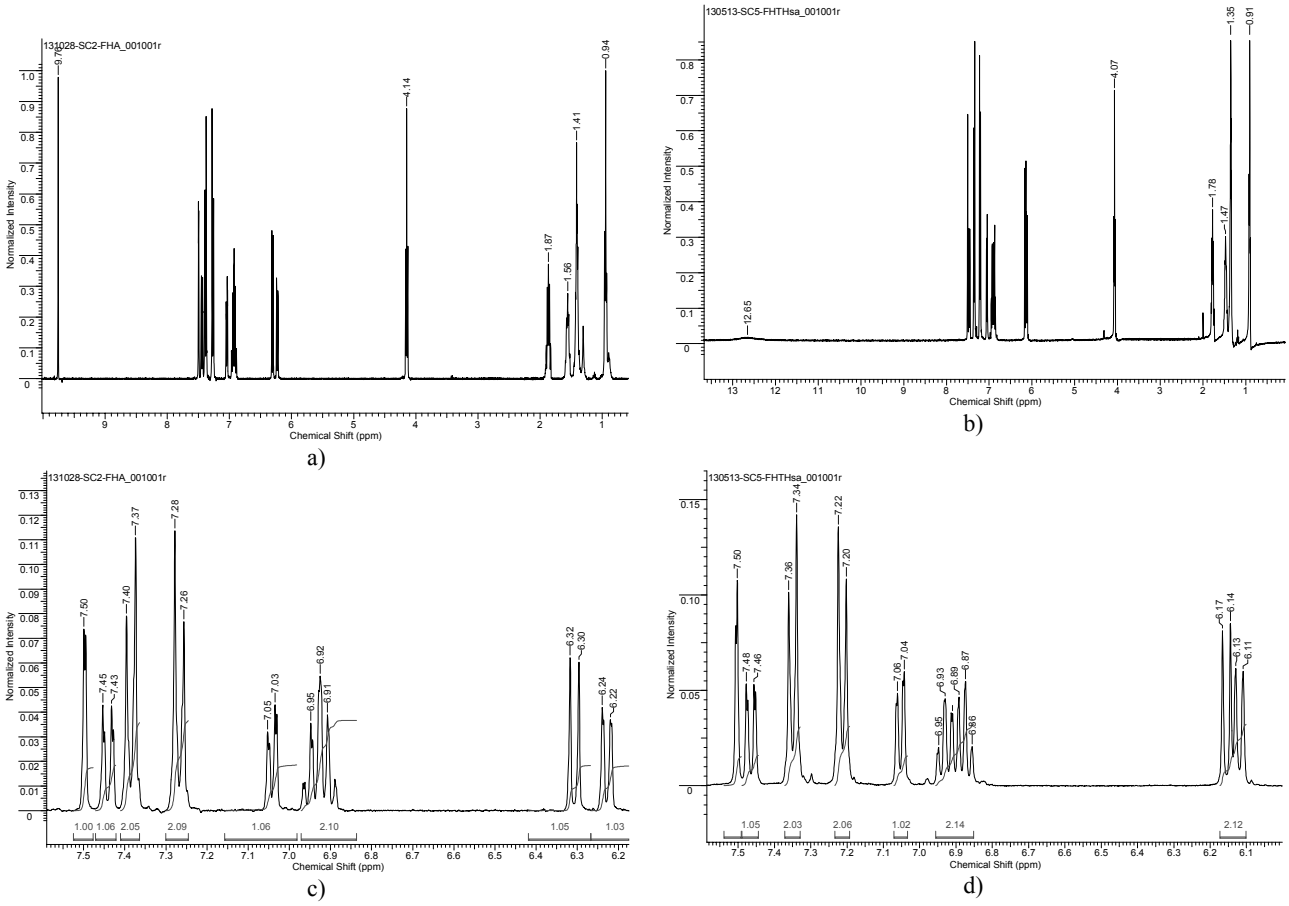
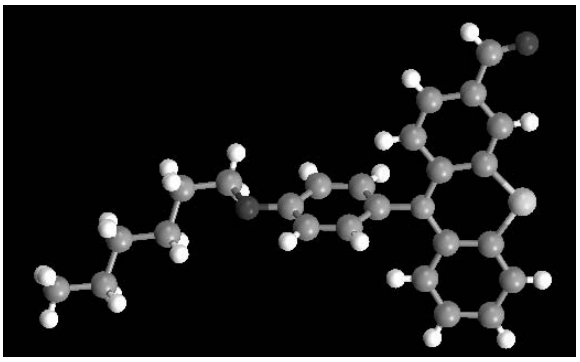


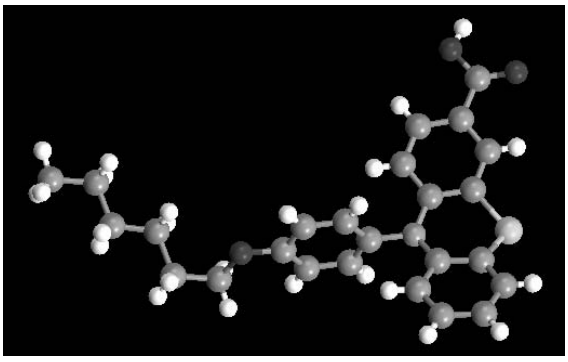
Fig. 2 – NMR spectra of the a), c) **1A** and b), d) **2Ac** and of their corresponding expanded aromatic regions.

The most incontestable evidence of carboxylic acid formation has been brought by **single crystal X-ray diffraction**, which clearly proves the right molecular structure and also gives valuable clues related to its supramolecular organization and consequently to its thermotropic and photophysical properties (Fig. 3).

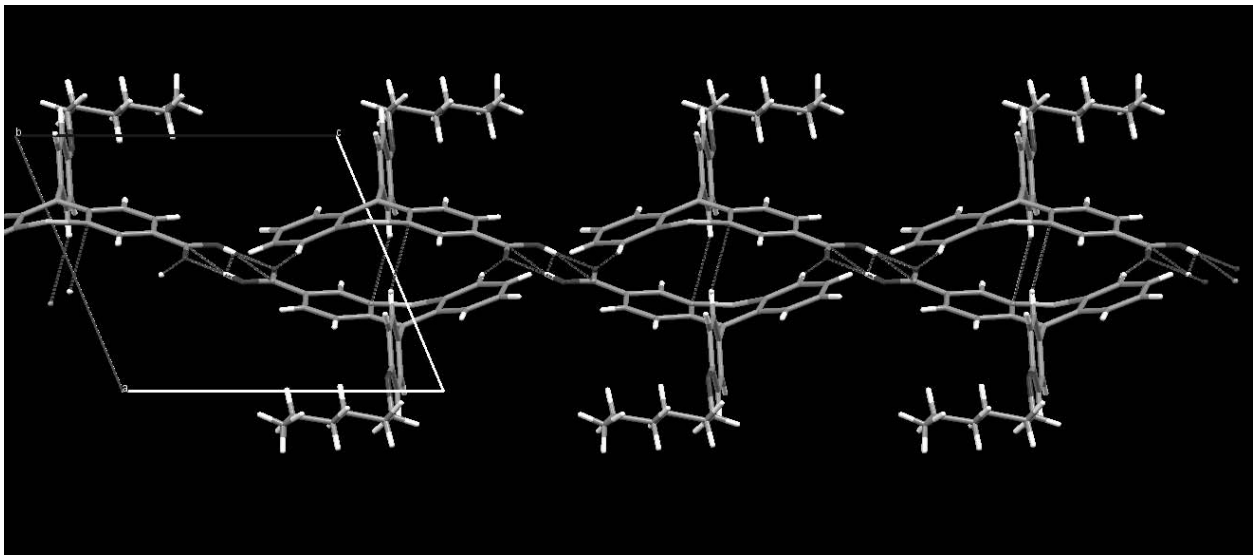
While the phenothiazine core has an almost planar configuration into the **1A** (Fig. 3a), it adopts the well-known butterfly architecture[4,21] into **2Ac** (Fig. 3b), consequence of the different electron-withdrawing effects of the two groups – carbonyl and carboxyl –, as also evidenced into the NMR spectra. Due to the steric hindrance, the oxyphenyl ring lays nearly perpendicular on the phenothiazine plane, which will further influence the photophysical properties. The presence of the carboxylic units prompts the forming of H-bonds leading to the appearance of dimers, and further to supramolecular ribbons (Fig. 3c). The H-bonds were also evidenced by FTIR spectra. These quite strong H-bonds lead to a close packing into the **2Ac** crystals. As can be observed from **polarized light microscopy** (POM) measurements[22,23], while the aldehyde derivative **1A** melts at 108-110 ^{o}C, the melting point increases almost 150 ^{o}C, at 248-253 ^{o}C, for the **2Ac** acid derivative. The strong H-bonds are also responsible for the easy crystallization[24,25] during the cooling of the acid derivative at high temperature (197 ^{o}C), while the aldehyde derivative was able to crystalize only once the room temperature (RT) was reached (Fig. 4).



a)

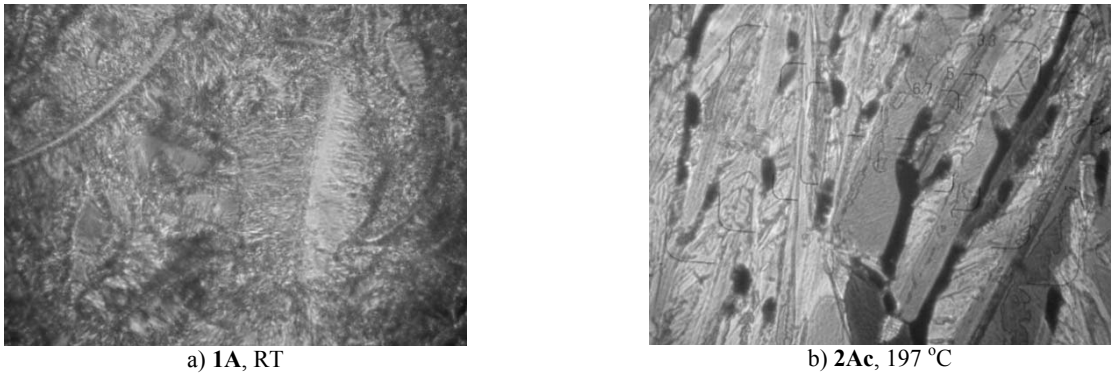


b)



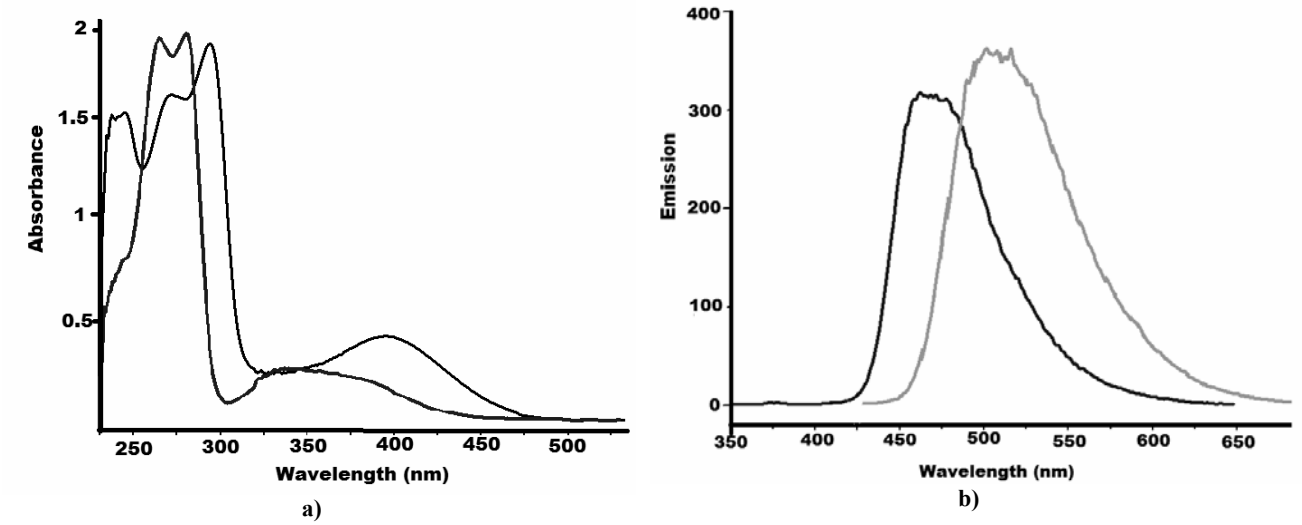
c)

Fig. 3 – Structure of a) **1A** and b) **2Ac**, and c) supramolecular structure of **2Ac**, as obtained by single crystal X-ray diffraction.



a) **1A**, RT b) **2Ac**, 197 °C

Fig. 4 – POM images of the **1A** and **2Ac** crystalline state reached during the cooling scan.



a) b)

Fig. 5 – a) UV-vis and b) photoluminescence spectra of the understudy phenothiazine derivatives (carboxylic derivative: blue line; aldehyde derivative: black and green lines, respectively).

The photophysical behavior of the two phenothiazine derivatives was monitored by UV-vis and photoluminescence spectroscopy, in diluted THF solution (10^{-5}M), in order to avoid any intermolecular interactions and to analyze the intrinsic behavior of the independent molecules. The compounds present two types of absorption bands (Fig. 5a), (i) one up to 300 nm – consisting in overlapped curves attributed to the π-π* transitions of the aromatic and heteroaromatic independent rings, while (ii) the second one, consisting in a broad band with absorption maximum over 300 nm, is attributed to the π-π* transitions of the conjugated core giving rise to an extended chromophore.[4,26] It can be observed that introduction of the carboxylic unit hypsochromically shifts the absorption with almost 50 nm, indicating a less extended conjugation as compared to the aldehyde substituent. This effect is also observed in the emission spectra (Fig. 5b), when the solutions are excited with light of wavelength corresponding to the absorption maximum of the conjugated chromophore. Thus, while the **1A** aldehyde derivative emits green light with emission maximum around 510 nm, the emission of the carboxylic derivative shifts in the blue light domain, with an emission maximum around 460 nm. It appears that the introduction of carboxylic unit is a facile pathway to obtain blue light emitters. It is remarkable that the emission curves are quite sharp, signature of a single fluorophore, increasing the potential of the pure light emission required by the organic opto-electronic devices.[27-29]

EXPERIMENTAL

Synthesis

0.254 g (2.5 mmol) t-BuOK and 5 ml dry THF were introduced into a Schlenk tube and cooled by immersing into an ice-bath. Then, 0.62 g (2 mmol) of diethyl-(3-hexyl-thiophen-2-yl)-methylphosphonate dissolved into 5 ml THF were added slowly under vigorous stirring, and the resulted mixture was kept at 0°C for 1 hour.

0.800 g (2mmol) of 10-(4-hexyloxyphenyl)-10H-phenothiazine -3-carbaldehyde dissolved in 10 ml dry THF were then added dropwise during 30 minutes and then the temperature of the reaction was left to reach slowly room temperature and kept under stirring overnight. The color of the reaction mixture changed from red to ochre. After the completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure, and the inorganic salts were washed with distilled water. The residue obtained after filtration was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate 9:1) to afford the understudy compound as fine crystals (0.415 g, 74% yield) which crystallized from ethyl acetate as single crystals suitable for X-ray diffraction.

The synthetic pathway performed in the absence of potassium t-butoxide did not proceed to the carboxylic acid compound, highlighting the importance of the salt in the oxidation reaction.

^{1}H NMR (acetone-d, 400 MHz, ppm): δ (ppm): 7.36, 7.33 (d, 2H), 7.29 (s, 1H), 7.23-7.19 (superposed signals, 3H); 7.07-7.02 (superposed signals, 3H), 6.95, 6.93, 6.91 (t, 1H), 6.87, 6.85, 6.83 (t, 1H), 6.75, 6.71 (d, 1H), 6.15, 6.13 (d, 1H), 6.11, 6.09 (d, 1H), 4.09, 4.08, 4.07 (t, 2H), 1.8 (m, 2H), 1.61-1.24 (superposed multiplets, 14H), 0.94 (t, 3H), 0.92 (t, 3H).

FT-IR (KBr, cm^{-1}): 3439 (ν_{O-H}), 3067, 3043 ($\nu_{CHaromatic}$), 2957, 2927, 2855 (ν_{CH3}, ν_{CH2}), 1730 ($\lambda_{C=O}$), 1606, 1575, 1508 ($\nu_{C=Caromatic}$), 1280 (ν_{C-O-C}, ν_{C-OH}), 824, 749 ($\delta_{CHaromatic}$).

10-(4-hexyloxyphenyl)-10H-phenothiazine-3-carbaldehyde

^{1}H NMR (400.13 MHz, DMSO-d_6, ppm) δ = 9.76 (s, 1H, H22), 7.50 (s, 1H, H4), 7.45, 7.43 (d, 1H, H2), 7. 7.40, 7.37 (d, 2H, H11, H15), 7.28, 7.26 (d, 2H, H12, H14), 7.05, 7.03 (d, 1H, H1), 6.97-6.89 (superposed bands, 2H, H7, H8), 6.32, 6.30 (d, 1H, H6), 6.23 (d, 1H, H9), 4.14 (t, 2H, H16), 1.90-1.83 (m, 2H, H17), 1.59-1.39 (superposed bands, 6H, H18, H19, H20), 0.94 (t, 3H, H21).

FT-IR (KBr, cm^{-1}): 3059, 3021 ($\nu_{CHaromatic}$), 2945, 2920, 2855 (ν_{CH3}, ν_{CH2}), 1675 ($\nu_{C=O}$), 1595, 1504 ($\nu_{C=Caromatic}$), 1239 (ν_{C-O-C}), 836, 813, 744 ($\delta_{CHaromatic}$).

Equipments

Infrared spectra were recorded on a FT-IR Bruker Vertex 70 Spectrophotometer in the transmission mode, by using KBr pellets. The NMR spectra were obtained on a Bruker Avance DRX 400 MHz Spectrometer equipped with a 5 mm QNP direct detection probe and z-gradients. The chemical shifts are reported as δ values (ppm) relative to the residual peak of the solvent. Crystallographic measurements were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated Mo Kα radiation, as previously described.[4,18] These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. UV–Vis absorption and photoluminescence spectra were recorded on a Carl Zeiss Jena SPECORD M42 spectrophotometer and a Perkin Elmer LS 55 spectrophotometer, respectively, in solution, using 10 mm quartz cells.

CONCLUSIONS

The carboxylic derivative of a phenothiazine compound has been obtained from the corresponding aldehyde *via* an oxidation process in the presence of tBuOK – an unreported reaction pathway. The structures of the new formed acid and of the aldehyde reagent were confirmed by FTIR and NMR spectroscopic methods and by single crystal X-ray diffraction. The photophysical study proved that transforming of the aldehyde to carboxylic group is an efficient way to blue shift the emission capability of the phenothiazine ring from green to blue region.

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