Dyes and Pigments 82 (2009) 26–30

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

A porphyrin derivative from cardanol as a diesel fluorescent marker

Siriorn Puangmalee [a], Amorn Petsom [b,c], Patchanita Thamyongkit [b,c,*]

[a] *Program in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*
[b] *Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand*
[c] *Research Center for Bioorganic Chemistry, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*

ARTICLE INFO

Article history:
Received 24 August 2008
Received in revised form
23 October 2008
Accepted 25 October 2008
Available online 6 November 2008

Keywords:
Porphyrin
Cardanol
Marker
Fluorescent marker
Fuel marker
Diesel marker

ABSTRACT

A novel porphyrin fluorescent marker from a naturally occurring substance, cardanol, is presented. Synthetic routes were investigated to obtain an aldehyde precursor derived from cardanol and the target porphyrin; the conditions for porphyrin formation, choice of acid and reaction time were optimized. The resulting *meso*-tetrakis(2-methoxy-4-pentadecylphenyl)porphyrin exhibits high solubility in diesel fuel and its strong fluorescence was observed as two characteristic signals; the porphyrin marker was stable in diesel for at least 3 months. The physical properties of the diesel were unaffected by the presence of the porphyrinic marker at a concentration of 2 ppm.

1. Introduction

Generally, fuel oils are taxed according to the government rates, depending on their type and application. The governments encounter many problems resulting from tax evasion by some fuel sellers, via smuggling illicit fuel into the country, diluting the higher-taxed fuel with hydrocarbons or the lower-taxed fuels, and using the low-taxed fuels for purposes critically requiring the higher-taxed ones. These issues cause a huge loss of revenue to the government and adverse effects to consumers. To avoid these problems, fuel markers are used for marking and identifying types of petroleum products in the market. Several marker systems have been used for a few decades [1]. However, major drawbacks of many markers are their low solubility in non-polar solvents or oils and low stability in oils or in long storage condition at high temperature. Recently, some compounds with fluorescence properties, for example phthalocyanines, naphthocyanines [1b], and coumarin derivatives [1c], were explored as "silent" fluorescent markers as they are visually invisible under ambient light but can be easily detected by their fluorescence. In addition, these compounds exhibit greater stabilities in petroleum products and their detection methods offer higher sensitivity, compared to the case of marker dyes. The important features of a fluorescent marker are: (1) solubility in petroleum products; (2) strong fluorescence in distinct regions from fluorescent components in petroleum products enabling them to be used at low concentrations; (3) invisibility to the naked eye; (4) stability in petroleum products for at least 3 months (the average shelf-life of the petroleum products); and (5) scalable syntheses.

Cardanol (**1a**–**d**, Chart 1) is a mixture of natural alkyl phenols obtained by vacuum distillation of cashew nut shell liquid (CNSL). Due to the solubility enhancement resulting from its solubilizing alkyl chain, several studies reported the introduction of cardanol into various macrocyclic frameworks such as fullerene [2], phthalocyanine [3] and porphyrins [4]. Synthetic tractability, high stabilities, and tunable photophysical properties make porphyrins attractive photosensitizing compounds. *Meso*-tetrasubstituted porphyrins can be simply prepared by acid-catalyzed pyrrole–aldehyde condensations, followed by oxidation of the porphyrinogen intermediate at ambient temperature and under atmospheric pressure [5]. Similar to other phenols, aromatic carbons of cardanol are susceptible to electrophilic aromatic substitution. Formylation of cardanol to obtain a starting aldehyde for the porphyrin formation was previously reported [6]. In this contribution, we explore the synthesis of a highly soluble porphyrin as a fluorescent marker for diesel from the naturally occurring cardanol. The study also includes development of a detection method for the porphyrin marker, investigation of effects of the marker on diesel properties, and stability test of the marker in diesel to evaluate the applicability of the porphyrin in the commercial diesel.

---

[*] Corresponding author. Research Center for Bioorganic Chemistry, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand. Tel.: +662 218 7587; fax: +662 254 1309.
E-mail address: patchanita.v@chula.ac.th (P. Thamyongkit).

0143-7208/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2008.10.015

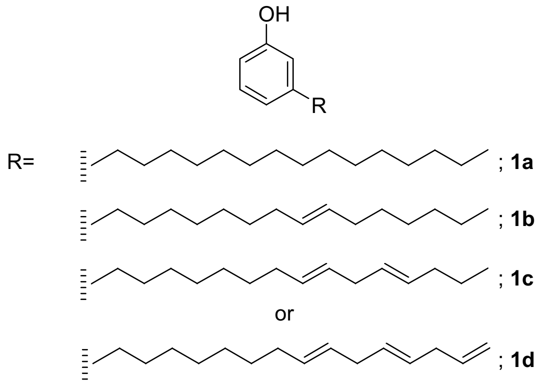


Chart 1.

2. Results and discussion

2.1. Syntheses of fluorescent markers

Generally, distillation of CNSL mainly gives a cardanol mixture of **1a**–**d** bearing a C_{15}-alkyl chain with 0–3 unsaturation sites [7]. Since the direct use of this cardanol mixture caused complications and side reactions of the olefinic double bonds in formylation and porphyrin formation (data not shown), hydrogenated cardanol was used (**1a**) [2]. Therefore, the synthesis started from formylation of hydrogenated cardanol **1a** by a reaction with paraformaldehyde in the presence of $SnCl_4$ and NEt_3 [6b], leading to aldehyde **2**. The conventional Reimer–Tiemann formylation afforded a mixture of both isomeric *o*-products. Initially, the target porphyrin was designed to contain *n*-pentadecyl groups at the *p*-positions and sterically encumbered hydroxyl groups at the *o*-positions of the meso-substituents providing the enhancement of the solubility of the macrocycle. An attempt to prepare the porphyrin by direct condensation of pyrrole and aldehyde **2** failed to give the desired porphyrin in a reasonable yield due to the difficulties encountered in the purification step. This observation is consistent with that reported in the literature [8]. Hence, methylation of phenol **2** was performed [9], leading to aldehyde **3** in 78% yield (Scheme 1).

Compound **3** was subjected to porphyrin formation. It has been known that rate and yield of porphyrin formation are dependent on nature of acid catalyst, its concentration, and of the reactant [10]. Herein, acid screening experiments were performed under TFA [5a], TFA/$BF_3 \cdot OEt_2$ [5d], or $BF_3 \cdot OEt_2$/NaCl/EtOH [11] catalysis, which are previously studied and widely used for porphyrin-forming reactions, as a function of condensation time from 0 to 45 min. The reaction progress was monitored according to the published procedure to obtain the appropriate time for porphyrin formation and, hence, to initiate the subsequent DDQ-oxidation step [10]. The yield of porphyrinic product was expressed by the intensity of its characteristic B-band at 420 nm. A representative plot of the yield of porphyrinic product as a function of condensation time is provided in Fig. 1.

According to the result shown in Fig. 1, the use of $BF_3 \cdot OEt_2$/NaCl/EtOH with the reaction time of 10 min was optimal for porphyrin production. Therefore, this condition was employed in the porphyrin formation step and upon the subsequent DDQ-oxidation, the desired porphyrin **4** was obtained in 35% yield (Scheme 2). In agreement with the result described by Stäubli et al. [12] for a series of simple porphyrins, the porphyrin **4** was obtained in a mixture of all four atropisomers bearing methoxy groups in four possible orientations relative to the porphyrin plane, i.e. $\alpha,\alpha,\alpha,\alpha$; $\alpha,\alpha,\alpha,\beta$; $\alpha,\alpha,\beta,\beta$ and $\alpha,\beta,\alpha,\beta$.

Porphyrin **4** exhibits satisfactory solubility in a variety of common organic solvents, such as toluene, hexanes and $CHCl_3$, and in diesel.

2.2. Detection and quantitative determination of fluorescent markers in diesel

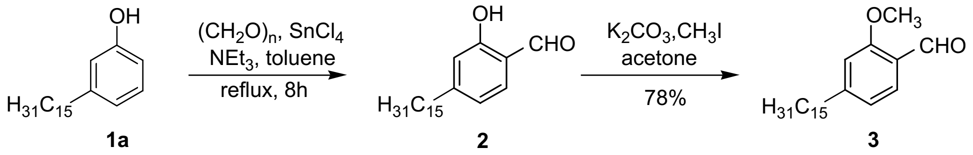
Porphyrin **4** shows a characteristic Soret band at 420 nm and Q-band at 512, 550, 590 and 645 nm. Its strong emission peaks at 652 and 719 nm are distinct from fluorescent impurities in diesel and serve as a twofold indicator for the marker. Furthermore, the intensity of these two peaks enables the quantification of porphyrin **4** in diesel, allowing us to evaluate the stability of porphyrin **4** in diesel. Hence, a standard calibration curve of porphyrin **4** in diesel was prepared by measuring fluorescence intensity at 652 nm ($\lambda_{exc} = 512$ nm) of a series of the solutions of **4** in diesel at the concentration range of 0–10 ppm and plotting it against the concentration. A standard calibration equation was found to be $Y = 58.35X$ with the correlation coefficient equal to 0.9984. Since the diesel is generally consumed within 3 months after releasing to the market, the stability test of porphyrin **4** in diesel was performed in a period of 3 months. The test was carried out by measuring fluorescence of a solution of **4** in diesel at the concentration of 2 and 5 ppm after 1–3 months and the fluorescence intensity at 652 nm was converted into the marker concentration by the above-mentioned calibration equation. At these concentrations of the marker, color of porphyrin is invisible to the naked eyes. The result is summarized in Table 1.

The result from Table 1 indicated that the fluorescence of porphyrin **4** remained intact for at least 3 months and, hence, porphyrin **4** is stable enough to be used as a marker in diesel.

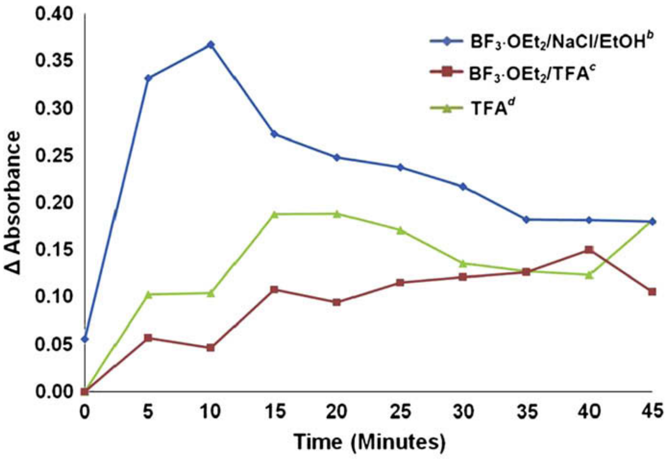
2.3. Effect of porphyrin 4 on physical properties of diesel

This part focuses on the investigation of physical properties of marked diesel to ensure that the addition of porphyrin **4** will not significantly affect the physical properties of the original diesel. Diesel from PTT Public Company Limited (PTT) containing fluorescent marker **4** was tested for the physical properties using the American Society for Testing and Materials (ASTM) methods. The physical properties of marked and unmarked diesel were compared as shown in Table 2.

The result from Table 2 revealed that the physical properties of marked diesel were similar to those of unmarked diesel and, thus, the presence of marker **4** does not significantly affect the physical properties of diesel.



Scheme 1.



[a] Condensations were performed with [pyrrole] = [aldehyde **3**] = 10 mM, at room temperature. [b] $[BF_3{\cdot}OEt_2]$ = 3.3 mM, [NaCl] = 250 mM, [EtOH] = 0.13 mM (as a stabilizer in $CHCl_3$) in $CHCl_3$. [c] $[BF_3{\cdot}OEt_2]$ = 0.32 mM, [TFA] = 15 mM in CH_2Cl_2. [d] [TFA] = 10 mM in CH_2Cl_2. [e] Δ Absorbance = maximum absorbance (at 420 nm) – absorbance at base

Fig. 1. Acid screening on pyrrole + aldehyde 3 condensation.[a]

3. Conclusion

In this study, cardanol was converted to an aldehyde starting material for the synthesis of porphyrin **4** through 2 simple quantitative steps. The optimization of the porphyrin formation step was performed spectroscopically by screening selected acid catalyst systems and reaction time. By the optimum condition obtained, porphyrin **4** was synthesized in satisfactory isolated yield. Porphyrin **4** proves itself as a considerable candidate for diesel fluorescent marker by its high solubility, distinct fluorescence and favorable stability in diesel without significantly affecting the physical properties of diesel.

4. Experimental section

4.1. Material and methods

All chemicals were obtained from commercial suppliers and used without further purification. $CHCl_3$ was stabilized with 0.8% ethanol. Melting point was measured on a Stuart Scientific Melting Point SMP1. ^1H NMR and ^{13}C NMR spectra were collected in deuterated chloroform ($CDCl_3$) using Varian Mercury NMR spectrometer at 400.1 MHz (^1H) and 100 MHz (^{13}C). Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual $CHCl_3$ peak (7.26 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR) and coupling constants (J) are reported in Hertz (Hz). Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) was measured with a Micromass (LCT) mass spectrometer and matrix-assisted laser-desorption ionization mass spectrometry (MALDI-MS) was performed by using dithranol as a matrix. Absorption spectrum of the marker was measured on a Perkin–Elmer (Lambda 2) UV/vis spectrophotometer. Fluorescence spectrum of the marker and the quantity of the fluorescent marker in diesel were measured on a Perkin Elmer LS 50 luminescence spectrophotometer. In regard to the physical properties of marked and unmarked diesels: kinematic viscosity was recorded on Cannon automatic viscometer; flash point (Pensky–Martens) was measured on a Perzoc ISL (PMFP93) automatic flash point tester; pour point was recorded on an ISL (CPP5GS) automatic pour point tester; sulfur content was determined using a Outokumpu (X-MET820) X-ray diffraction spectrometer; distillation was performed with a AD 865G (ISL) automatic distillation apparatus; total acidity was evaluated with a Metrohm 665 total acid number analyzer and color was observed with a Lovibond (PFX990/P) petrochemical tintometer.

4.2. Non-commercial compounds

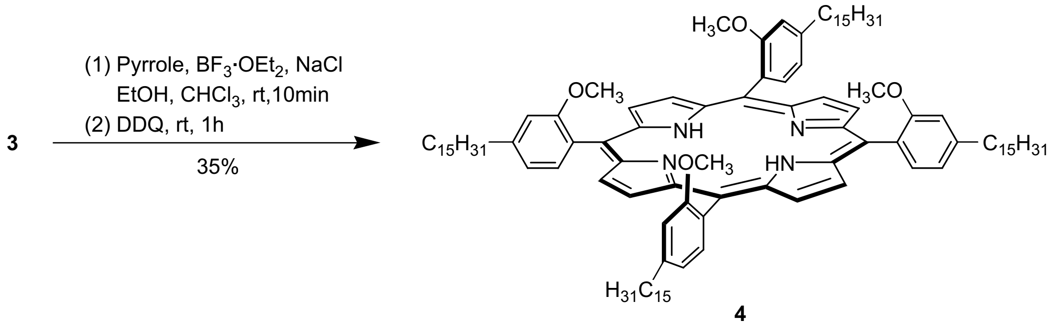
Hydrogenated cardanol (**1a**) was kindly supplied by Dr. Nantanit Wanichacheva and 2-hydroxy-4-pentadecylbenzaldehyde (**2**) was obtained by a literature procedure [6b].

4.2.1. 2-Methoxy-4-pentadecylbenzaldehyde (3)

Following a previously published procedure [6b], a solution of compound **2** (192 mg, 0.577 mmol) in acetone (5 mL) was treated with K_2CO_3 (114 mg, 0.692 mmol) in a 50-mL round bottom flask. After stirring at room temperature for 10 min, the reaction mixture was treated with iodomethane (43.1 μL, 0.692 mmol) and stirred further until no more substrate was observed by TLC monitoring (about 14 h). The mixture was washed with distilled water (2 × 20 mL) and extracted with ethyl acetate (2 × 20 mL) in a separating funnel. The organic phase was separated, dried over anhydrous Na_2SO_4 and filtered. After the removal of solvent, the resulting crude product was purified by column chromatography (silica, hexanes) to give white crystals (162 mg, 78%). m.p. 39–40 °C; ^1H NMR: δ 0.87 (t, $J = 6.8$ Hz, 3H), 1.20–1.45 (m, 24H), 1.55–1.65 (m, 2H), 2.62 (t, $J = 7.8$ Hz, 2H), 3.90 (s, 3H), 6.77 (s, 1H), 6.83 (d, $J = 7.8$ Hz, 1H), 7.72 (d, $J = 7.8$ Hz, 1H), 10.39 (s, 1H); ^{13}C NMR: δ 14.0, 20.7, 22.5, 29.19, 29.24, 29.3, 29.4, 29.5, 29.6, 29.77, 29.80, 29.83, 30.9, 31.8, 36.5, 55.5, 111.5, 120.9, 122.7, 128.6, 152.4, 161.9, 189.5; ESI-MS obsd 347.232; HR-ESI-TOF-MS obsd 347.2941, calcd 347.2950 $[(M+H)^+$; $M = C_{23}H_{38}O_2]$.

4.2.2. Synthesis of meso-tetrakis(2-methoxy-4-pentadecylphenyl)porphyrin (4)

4.2.2.1. Effects of acid catalyst and time on porphyrin formation. Following a previously published procedure [11], a solution



Scheme 2.

Table 1
The concentration of **4** in diesel after 1–3 months.

Month	Concentration of **4**[a] (ppm)	
	2-ppm sample	5-ppm sample
1	2.02±0.02	4.97±0.01
2	2.02±0.01	4.97±0.01
3	2.02±0.01	4.97±0.01

[a] Average ± standard deviation, $n = 2$.

of **3** (200 mg, 0.577 mmol) and pyrrole (39.9 μL, 0.577 mmol) in $CHCl_3$ (58 mL) was degassed with N_2 for 10 min and then treated with $BF_3 \cdot OEt_2$ (24.1 μL, 0.190 mmol) and NaCl (847 mg, 14.5 mmol) at room temperature. Aliquots (2 μL) were taken from a reaction vessel via syringe every 5 min for 45 min reaction time and injected into a solution of DDQ in toluene (300 μL, 0.010 M). This solution was diluted in CH_2Cl_2/EtOH (3 mL, 3:1) and absorption spectra were recorded instantaneously.

Monitoring the reaction under $BF_3 \cdot OEt_2$/TFA and TFA catalysis was performed in the same manner by using $BF_3 \cdot OEt_2$ (2.4 μL, 0.019 mmol) and TFA (64.6 μL, 0.870 mmol) for the former case, and TFA (43.1 μL, 0.580 mmol) for the latter one. CH_2Cl_2 was used instead of $CHCl_3$ in both catalysis conditions. A graph between absorbance (y-axis) and time (x-axis) was plotted for all three acid catalytic systems.

*4.2.2.2. Synthesis of compound **4** under optimized condition.* Following the above-mentioned procedure for the acid screening experiment under $BF_3 \cdot OEt_2$/NaCl/EtOH cocatalysis, the identical amount of **3**, pyrrole, $BF_3 \cdot OEt_2$ and NaCl was reacted in $CHCl_3$ at room temperature for 10 min. DDQ (98.5 mg, 0.434 mmol) was added and the mixture was stirred at room temperature for an additional hour. The reaction mixture was filtered through a pad of silica, concentrated and then chromatographed (silica, CH_2Cl_2). Precipitation from hexanes/$CHCl_3$ furnished a purple solid (80 mg, 35%). ^1H NMR: δ −2.63 (br s, 2H), 0.87–0.90 (m, 12H), 1.20–1.63 (m, 96H), 1.86–1.96 (m, 8H), 2.93 (t, $J = 7.8$ Hz, 8H), 3.58, 3.55, 3.52 (3s, relative intensity = 1:2:1, 12H), 7.12 (m, 8H), 7.82, 7.86, 7.91 (3d, $J = 7.8$ Hz, relative intensity = 1:2:1, 4H), 8.72 (s, 8H); ^{13}C NMR: δ 14.2, 22.7, 29.4, 29.6, 29.66, 29.73, 29.8, 30.07, 30.11, 31.7, 31.9, 32.0, 36.5, 55.80, 55.83, 111.0, 111.1, 115.5, 115.6, 119.3, 128.5, 128.6, 135.4, 135.5, 144.7, 159.2, 159.3, 159.30, 159.34; MALDI-MS (dithranol): 1576.370; calcd avg mass 1576.435 ($C_{108}H_{158}N_4O_4$); λ_{abs} (CH_2Cl_2) 420, 512, 546, 589, 645 nm; λ_{em} ($\lambda_{ex} = 550$ nm, CH_2Cl_2) 652, 717 nm.

Table 2
Physical properties of marked and unmarked diesels.

Physical property	Method[a] (ASTM)	Diesel[b]	
		Unmarked	Marked
API[c] gravity at 15.6 °C	D 1298	38.64	38.64
Specific gravity at 15.6/15.6 °C	D 1298	0.83168	0.83168
Calculated cetane index[d]	D 976	56.0	56.0
Kinematic viscosity at 40 °C (cSt)	D 445	2.994	2.989
Pour point (°C)	D 97	−4.0	−4.0
Flash point (°C)	D 93	65.0	65.0
Sulfur content (w/w%)	D 4294	0.030	0.030
Distillation	D 86		
IBP[e] (°C)		173.0	173.0
10% (v/v) recovery (°C)		201.8	202.4
50% (v/v) recovery (°C)		280.1	279.7
90% (v/v) recovery (°C)		353.3	353.2
Color	D 1500	<0.5	<0.5

[a] Diesel was marked with porphyrin **4** at 5 ppm.

[b] American Society for Testing and Materials (ASTM).

[c] American Petroleum Institute (API).

[d] Calculated Cetane Index $= 454.74 - 1641.146D + 774.74D^2 - 0.554B + 97.803 (\log B)^2$; wherein D = Density at 15 °C, g/mL and B = 50% vol. Distillation, °C.

[e] Initial boiling point (IBP).

*4.3. Effect of fluorescent marker **4** on physical properties of diesel*

A diesel sample employed in this study was obtained from PTT. A 500-ppm stock solution of marker **4** was prepared by dissolving **4** (25 mg) in the diesel and made up to 50 mL in a volumetric flask. This solution (10 mL) was diluted 100 times by diesel to obtain a 5-ppm solution of marked diesel (1 L) for testing. Physical properties of marked and unmarked diesels were investigated according to the ASTM methods.

4.4. Quantitative determination of fluorescent marker in diesel

A series of calibration solutions of **4** in diesel were prepared at the concentration of 2, 4, 6, 8 and 10 ppm by pipetting the 500-ppm stock solution (0.2, 0.4, 0.6, 0.8 and 1.0 mL, respectively) into each 50-mL volumetric flask and made up to the volume with the diesel. Fluorescent spectra ($\lambda_{ex} = 512$ nm) were collected on a spectrofluorometer and a calibration curve between intensity (y-axis) and the concentration (x-axis) of fluorescent markers in diesel was plotted to give a calibration equation. This equation was used to quantify marker **4** in the stability test described below.

*4.5. Stability test of fluorescent marker **4** in diesel*

The test was performed with the diesel marked with compound **4** in the concentration of 2 and 5 ppm on a spectrofluorometer. The 2-ppm marked diesel was prepared according to the preparation of the 5-ppm one described above by diluting the 500-ppm stock solution of marker **4** (1 mL) in diesel in a 250-mL volumetric flask. Each solution was placed into 6 tightly sealed vials (5 mL each) and stored in an ambient environment. Each two solutions of each concentration were directly taken from the vials to the fluorescence measurement ($\lambda_{ex} = 512$ nm) after 1–3 months. Quantity of marker **4** was determined by the calibration equation.

Acknowledgments

This research was partially supported by Thai Research Fund (MRG4980059), Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials (NCE-PPAM) and Graduate School, Chulalongkorn University. Physical properties data of the marked and unmarked diesels were obtained at the PTT. Hydrogenated cardanol was a gift from Dr. Nantanit Wanichacheva.

Appendix. Supplementary data

Supporting information available for spectral data, including ^1H NMR spectra, ^{13}C NMR spectra and mass spectra for new compounds, and absorption and emission spectra of porphyrin **4**, as well as the calibration curve of porphyrin **4** in diesel. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.dyepig.2008.10.015.

References

[1] Selected publications: (a) Orelup RB. Chem Abstr 1988;103:114598;
(b) Krutak JJ, Cushaman MR, Waever MA. US Patent No. 5525516; 1996 Chem. Abstr 1996;125:37859n;
(c) Friswell MR. US Patent No. 5156653; 1992.

[2] Attanasi OA, Del Sole R, Filippone P, Ianne R, Mazzetto SE, Mele G, et al. Synlett 2004;5:799–802.

[3] Attanasi OA, Ciccarella G, Filippone P, Mazzetto SE, Mele G, Spadavecchia J, et al. J Porphyrins Phthalocyanines 2003;7:52–7.

[4] (a) Mele G, Sole RD, Vasapollo G, Garcıa-Lopez E, Palmisano L, Mazzetto SE, et al. Green Chem 2004;6:604–8;
(b) Attanasi OA, Del Sole R, Filippone P, Mazzetto SE, Mele GJ, Vasapollo G. J Porphyrins Phthalocyanines 2004;8:1276–84;
(c) Guo YC, Xiao WJ, Mele G, Martina F, Margapoti E, Mazzetto SE, et al. J

Porphyrins Phthalocyanines 2006;10:1071–9;
(d) Guo YC, Mele G, Martina F, Margapoti E, Vasapollo G, Xiao WJ. J Organomet Chem 2006;691:5358–90.

[5] (a) Lindsey JS, Schreiman IC, Hsu HC, Kearney PC, Marguerettaz AM. J Org Chem 1987;52:827–36;
(b) Lindsey JS, Wagner RW. J Org Chem 1989;54:828–36;
(c) Li F, Yang K, Tyhonas JS, MacCrum KA, Lindsey JS. Tetrahedron 1997;53:12339–60;
(d) Geier III GR, Ciringh Y, Li F, Haynes DM, Lindsey JS. Org Lett 2000;2:1745–8;
(e) Geier III GR, Riggs JA, Lindsey JS. J Porphyrins Phthalocyanines 2001;5:681–90.

[6] (a) Seidl PR, Pinto ADC, Menzel AR, Couto RO. US Patent No. 6673969; 2004 (b) Payne P, Tyman JHP, Mehet SK, Ninagawa A. J Chem Res 2006;6:402–5.

[7] Menon ARR, Pillai CKS, Sudha JD, Mathew AG. J Sci Ind Res 1985;44:324–38.

[8] Momenteau M, Mispelter J, Loock B, Bisagni E. J Chem Soc Perkin Trans 1 1983:189–96.

[9] Svelle S, Stein Kolboe S, Olsbye U, Swang O. J Phys Chem B 2003;107:5251–60.

[10] Geier III GR, Lindsey JS. Tetrahedron 2004;60:11435–44.

[11] Thamyongkit P, Specbacher M, Diers JR, Kee HL, Kirmaier C, Bocian DF, et al. J Org Chem 2004;69:3700–10.

[12] Stäubli B, Fretz H, Piantini U, Woggon W-D. Helv Chim Acta 1987:1173–93.