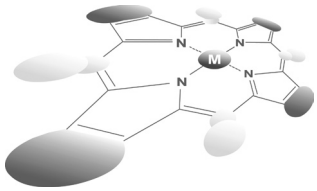
Journal of Porphyrins and Phthalocyanines
J. Porphyrins Phthalocyanines 2011; **15**: 560–574
DOI: 10.1142/S1088424611003471

Published at http://www.worldscinet.com/jpp/



Room temperature ionic liquids based on cationic porphyrin derivatives and tetrakis(pentafluorophenyl)borate anion

Hai-Jun Xu[a], Claude P. Gros[a◊], Stéphane Brandès[a], Pei-Yu Ge[b], Hubert H. Girault[b◊] and Jean-Michel Barbe*[a◊]

[a] *Université de Bourgogne, ICMUB (UMR 5260), 9, Avenue Alain Savary, BP 47870, 21078 Dijon Cedex, France*
[b] *Laboratoire d'Electrochimie Physique et Analytique, Station 6, Ecole Polytechnique Fédérale de Lausanne, Station 6, CH-1015 Lausanne, Switzerland*

Dedicated to Professor Karl M. Kadish on the occasion of his 65th birthday

Received 15 April 2011
Accepted 16 May 2011

ABSTRACT: A series of 11 low melting ionic liquids based on *meso*-substituted A_3B-porphyrins and A_2B_2-porphyrins containing one or two pyridyl substituents have been synthesized in high yields. Three of them are liquids at room temperature. All these porphyrinic salts were characterized by ^{1}H NMR, ^{19}F NMR, MALDI-TOF mass spectrometry, elemental analysis and UV-visible spectroscopy. The thermal properties and conductivity values of these salt derivatives have been also measured. A specific conductivity value of up to 4 mS.cm^{-1} could be obtained for a compound having the counter-anion $B(C_6F_5)_4^-$.

KEYWORDS: RT ionic liquids, A_3B-porphyrins, A_2B_2-porphyrins, conductivity, tetrakis(pentafluorophenyl)borate anion, DSC, TGA.

INTRODUCTION

Ionic liquids (ILs) are a group of organic salts that possess low melting point and usually afford liquids at temperatures below 100 °C [1]. Generally, ionic liquids consist completely of an organic cation and an anion (inorganic or organic). The ionic liquids which are free-flowing liquids at room temperature, can be called *Room Temperature Ionic Liquids* (RTILs) [1]. In recent years, ionic liquids have attracted much attention in many fields due to their unique chemical and physical properties such as air and moisture stability, high thermal stability, good electrical conductivity, high solubility, and no vapor pressure [1–9]. The ILs have been successfully used in many applications, including replacing traditional organic solvents in organic and inorganic syntheses [10], liquid-liquid extractions [11, 12], catalysis, electrochemical reactions [13, 14] as well as green solvents for lithium ion batteries [15–18] and for various reactions [19–21]. Up to now, most of the reported ILs are mainly based on 1,3-dialkylimidazolium cations, 1-alkylpyridinium cations and quaternary ammonium salts, whereas anions are mainly focused on $[BF_4]^-$, $[PF_6]^-$, $[CF_3SO_3]^-$, $[(CF_3SO_2)_2N]^-$ and $[RCO_2]^-$ [1, 22–26]. However, there are only few examples where tetrakis(pentafluorophenyl)borate anion has been used in ILs [27], despite the fact that it can decrease the melting point of the salts due to its weak anion coordination properties, bulkiness and benefit to a good charge distribution [1].

In addition, porphyrins have also aroused remarkable and extensive interest for many years due to their wide-ranging applications in photophysics [28], coordination chemistry [29], liquid crystals [30], solar cells [31, 32], catalysis [33, 34], photovoltaic devices [35], photodynamic therapy (PDT) [36] and artificial light-harvesting antennas [37]. The excellent properties of ionic liquids and porphyrins stimulated us to develop ionic liquid

◊SPP full member in good standing

*Correspondence to: Jean-Michel Barbe, email: jean-michel.barbe@u-bourgogne.fr, tel: +33 (0)3-80-39-61-19, fax: +33 (0)3-80-39-61-17

porphyrin derivatives based on tetrakis(perfluorophenyl)-borate salts and cationic porphyrins. The room temperature liquid state was attained by introducing long alkoxy chains on the *meso* phenyl groups of the porphyrins. During the progress of our work, Gryko and coworkers reported the synthesis of *meso*-substituted liquid porphyrins [38]. Concomitantly, Maruyama and coworkers independently reported the synthesis of room temperature liquid porphyrins [39]. Here, we report the first trial way to synthesize one of the most versatile ionic liquids. These ionic liquid porphyrins (Chart 1) have been examined by ^{1}H and ^{19}F NMR, MALDI-TOF mass spectrometry, elemental analysis, DSC, TGA and UV-visible spectroscopy. Room temperature conductivity measurements have also been performed.

EXPERIMENTAL

Instrumentation

^{1}H and ^{19}F NMR spectra were recorded with a Bruker DRX-300 AVANCE transform spectrometer at the "*Plateforme d'Analyse Chimique de l'Université de Bourgogne*" (PACSMUB); chemical shifts are expressed in ppm relative to chloroform. UV-vis spectra were recorded with a Varian Cary 1 spectrophotometer. Mass spectra and accurate mass measurements (HRMS) were obtained with a Bruker Daltonics Ultraflex II spectrometer in the MALDI/TOF reflectron mode by using dithranol as a matrix. Accurate mass measurements (HRMS) were carried out under the same conditions as before by using the PEG-ion series as an internal calibrant. Both measurements were made at the PACSMUB.

Thermogravimetric (TGA) measurements were performed on a Netzsch STA 409 PC Luxx analyzer at the ICMUB Institute. Samples were purged in an Ar (30 $mL.min^{-1}$)/O_2 (10 $mL.min^{-1}$) stream during analysis and heated to 900 °C in alumina crucibles with a heating rate of 10 $K.min^{-1}$. Differential Scanning Calorimetry (DSC) measurements were performed on a Perkin Elmer Diamond DSC instrument. The DSC measurements were carried out under nitrogen at atmospheric pressure in a sealed Al pan with a heating rate of 5 K/min or 10 K/min at the "Ecole Polytechnique Fédérale de Lausanne, EPFL". Resistance of ionic liquid porphyrin was detected by an on-chip conductivity sensor connected to an AutoLab PGSTAT 12 potentiostat at EPFL.

Chemicals and reagents

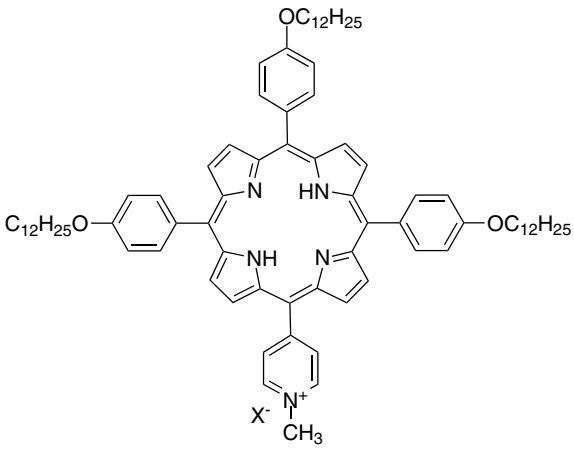
Unless otherwise noted, all chemicals and solvents were of analytical reagent grade and used as received. Absolute dichloromethane (CH_2Cl_2) was obtained from Carlo Erba. Silica gel (Merck; 70–120 mm) was used for column chromatography. Analytical thin-layer chromatography was performed with Merck 60 F254 silica gel (precoated sheets, 0.2 mm thick). Reactions were monitored by thin-layer chromatography and UV-vis spectroscopy. The 4-(dodecyloxy)benzaldehyde (**2a**) [40, 41] and 5-(4-pyridyl)-dipyrromethane [42] were synthesized according to the respective reported literature methods.

3,4,5-tris(dodecyloxy)benzaldehyde (2b). A mixture of 3,4,5-trihydroxybenzaldehyde (1.54 g, 10 mmol), 1-bromododecane (14.95 g, 60 mmol), K_2CO_3 (4.16 g, 30 mmol), and KI (100 mg) in DMF (60 mL) was stirred at 70 °C for 16 h. The reaction mixture was cooled to room temperature and mixed with water. The resulting aqueous layer was extracted three times with chloroform. The organic layers were combined, then washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting crude product was purified by column chromatography (silica gel, eluent $CHCl_3$/heptane 2/3) followed by recrystallization from $CHCl_3$/MeOH. The product was obtained as a white solid (6.26 g, yield: 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 9.85 (s, 1H, -CHO), 7.10 (s, 2H, phenyl-H), 4.06 (m, 6H, OCH_2-), 1.87 (m, 6H, OCH_2-CH_2-), 1.47 (m, 6H, OCH_2-CH_2-CH_2-), 1.29 (m, 48H, -$(CH_2)_9$-), 0.90 (t, 9H, J = 6 Hz).

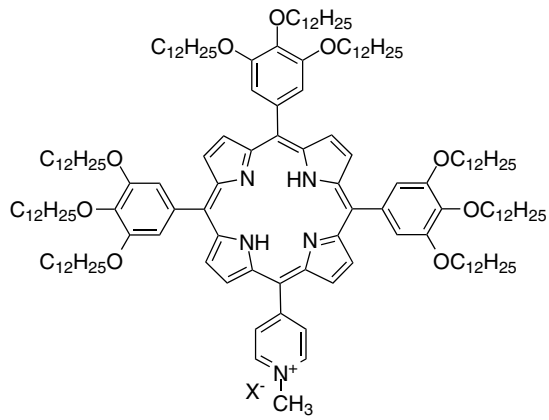
5-(4-pyridyl)-10,15,20-tris(4-dodecyloxyphenyl)-porphyrin (3a) and 5,15-di(4-pyridyl)-10,20-bis(4-dodecyloxyphenyl)porphyrin (4a). 4-(dodecyloxy)-benzaldehyde (2.35 mmol, 1.548 g) and 4-pyridine-dipyrromethane (2.35 mmol, 0.524 g) were dissolved in propionic acid (30 mL) in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a water-cooled reflux condenser. The mixture was then allowed to reflux for 2.5 h under air in the dark. After cooling, the reaction mixture was slowly poured into a 1/1 (v/v) mixture of methanol (60 mL) and cold (<5 °C) aqueous NH_4OH (60 mL) was added. Filtration and washing with cold water gave a black solid. The resulting residue was purified by silica-gel column chromatography repeatedly with 100% CH_2Cl_2, 2% MeOH/CH_2Cl_2 to afford 5,10,15,20-tetra-[4-(dodecyloxy)phenyl]porphyrin as the first band (very small amount), the porphyrin **3a** (130 mg, yield: 14% based on dipyrromethane) as the second band and the porphyrin **4a** (175 mg, yield: 15%) as the third band.

5-(4-pyridyl)-10,15,20-tris(4-dodecyloxyphenyl)-porphyrin (3a). ^{1}H NMR ($CDCl_3$): δ, ppm 9.05 (d, 2H, J = 6 Hz, pyridyl-H), 8.93 (m, 6H, pyridyl-H and β-pyrrole-H), 8.80 (d, 2H, J = 6 Hz, β-pyrrole-H), 8.19 (d, 2H, J = 6 Hz, β-pyrrole-H), 8.13 (d, 6H, J = 9 Hz, phenyl-H), 7.30 (d, 6H, J = 9 Hz, phenyl-H), 4.27 (t, 6H, J = 6 Hz, O-CH_2-), 1.99 (m, 6H, O-CH_2-CH_2-), 1.64 (m, 6H, -O-CH_2-CH_2-CH_2-), 1.43 (m, 48H, -$(CH_2)_8$-), 0.92 (m, 9H, -CH_3), -2.75 (s, 2H, NH). HR-MS (MALDI-TOF): m/z 1168.8084 $[M + H]^+$ 1168.7977 calcd. for $C_{79}H_{102}N_5O_3$. UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-3}$ $M^{-1}.cm^{-1}$) 421 (1769), 517.0 (71), 555.0 (46), 592.1 (26), 650.0 (27).

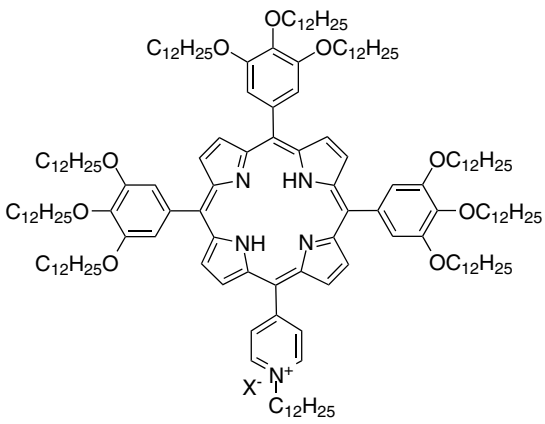
5,15-di(4-pyridyl)-10,20-bis(4-dodecyloxyphenyl)-porphyrin (4a). ^{1}H NMR ($CDCl_3$): δ, ppm 9.06 (d, 4H,



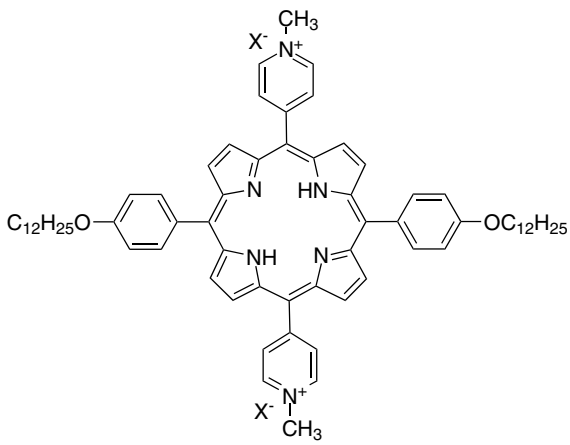
5a: $X^- = I^-$
6a: $X^- = B(C_6F_5)_4^-$



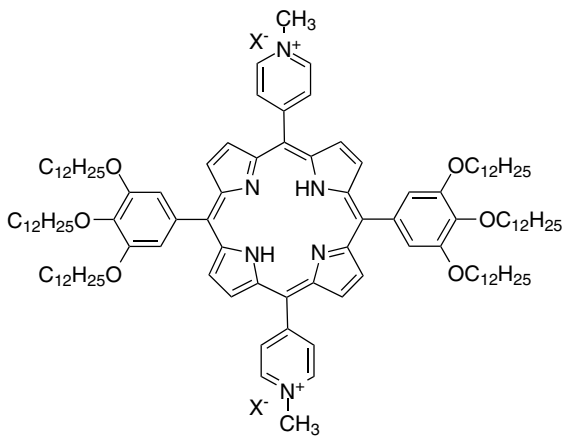
5b: $X^- = I^-$
6b: $X^- = B(C_6F_5)_4^-$



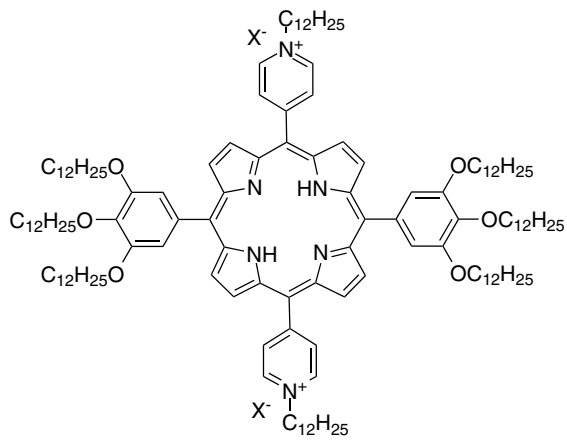
7: $X^- = Br^-$
8: $X^- = B(C_6F_5)_4^-$



9a: $X^- = I^-$



9b: $X^- = I^-$
10: $X^- = B(C_6F_5)_4^-$



11: $X^- = Br^-$
12: $X^- = B(C_6F_5)_4^-$

Chart 1. Structures of compounds **5**–**12**

J = 6 Hz, pyridyl-H), 8.97 (d, 4H, *J* = 6 Hz, pyridyl-H), 8.83 (d, 4H, *J* = 3 Hz, β-pyrrole-H), 8.18 (d, 4H, *J* = 6 Hz, β-pyrrole -H), 8.12 (d, 4H, *J* = 9 Hz, phenyl-H), 7.31 (d, 4H, *J* = 6 Hz, phenyl-H), 4.27 (t, 4H, *J* = 6.0 Hz, O-*CH*$_2$-), 2.04 (m, 4H, O-CH$_2$-*CH*$_2$-), 1.66 (m, 4H, -O-CH$_2$-CH$_2$-*CH*$_2$-), 1.44 (m, 32H, -(*CH*$_2$)$_8$-), 0.93 (t, 6H, *J* = 6 Hz, -*CH*$_3$), -2.79 (s, 2H). MS (MALDI-TOF): *m/z* 985.61 [M + H]$^+$, 985.61 calcd. for $C_{66}H_{77}N_6O_2$. UV-vis (2%CH_3OH in CH_2Cl_2): λ_{max}, nm (ε × 10^{-3} $M^{-1}.cm^{-1}$) 420.0 (1622), 515.0 (72), 552.0 (37), 591.0 (23), 650.0 (18).

5-(4-pyridyl)-10,15,20-[3,4,5-tris(dodecyloxy)phenyl]porphyrin (3b) and 5,15-dipyridyl-10,20-bis[3,4,5-tris(dodecyloxy)phenyl]porphyrin (4b). The reaction was carried out using the same procedure as for **3a** and **4a** starting from 3,4,5-tris(dodecyloxy)benzaldehyde (2.35 mmol, 1.548 g) and 4-pyridinedipyrromethane (2.35 mmol, 0.524 g). The resulting residue was purified by silica-gel column chromatography three times with 100% CH_2Cl_2, 25% $CHCl_3$-75% CH_2Cl_2 to afford the purple porphyrin **3b** as the second red band and the purple porphyrin **4b** as the third red band which were both recrystallized from chloroform/methanol to give the pure porphyrin **3b** (143 mg, yield: 8%, according to the dipyrromethane) and the pure porphyrin **4b** (182 mg, yield: 9%) respectively.

5-(4-pyridyl)-10,15,20-tris[3,4,5-tris(dodecyloxy)phenyl]porphyrin (3b). ^{1}H NMR ($CDCl_3$): δ, ppm 9.00 (m, 8 H, pyridyl-H, β-pyrrole-H), 8.79 (d, 2H, *J* = 6 Hz, β-pyrrole-H), 8.16 (d, 2H, *J* = 6 Hz, β-pyrrole-H), 7.45 (s, 6H, phenyl-H), 4.33 (t, 6H, J_{HH} = 6 Hz, O-*CH*$_2$-), 4.12 (t, 12 H, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 6.3 Hz, O-*CH*$_2$-), 2.07 (m, 6H, O-CH$_2$-*CH*$_2$-), 1.88 (m, 12H, O-CH$_2$-*CH*$_2$-), 1.72–1.25 (m, 162H, -(*CH*$_2$)$_9$-), 0.90 (m, 27H, -CH$_3$), -2.80 (s, 2H, NH). MS (MALDI-TOF): *m/z* 2273.75 [M + H]$^+$, 2273.89 calcd. for $C_{151}H_{246}N_5O_9$. UV-vis (CH_2Cl_2): λ_{max}, nm (ε × 10^{-3} $M^{-1}.cm^{-1}$) 421.0 (350), 516.0 (18), 552.0 (8.7), 591.0 (4.8), 649.0 (4.2).

5,15-di-(4-pyridyl)-10,20-bis[3,4,5-tris(dodecyloxy)phenyl]porphyrin (4b). ^{1}H NMR ($CDCl_3$): δ, ppm 9.06 (m, 8 H, pyridyl-H), 8.83 (d, 4H, *J* = 3 Hz, β-pyrrole-H), 8.19 (d, 4H, *J* = 6 Hz, β-pyrrole-H), 7.45 (s, 6H, phenyl-H), 4.33 (t, 4H, *J* = 6 Hz, O-*CH*$_2$-), 4.12 (t, 8H, *J* = 6 Hz, O-*CH*$_2$-), 2.01 (m, 4H, O-CH$_2$-*CH*$_2$-), 1.90 (m, 8H, O-CH$_2$-*CH*$_2$-), 1.25–1.67 (m, 108 H, -(*CH*$_2$)$_9$-), 0.95–0.85 (m, 18H), -2.82 (s, 2H). HR-MS (MALDI-TOF): *m/z* 1722.3385 [M + H]$^+$, 1722.3411 calcd. for $C_{114}H_{173}N_6O_6$. UV-vis (CH_2Cl_2): λ_{max}, nm (ε × 10^{-3} $M^{-1}.cm^{-1}$) 421.0 (448.9), 516.0 (22.7), 550.0 (8.8), 591.0 (7.0), 646.0 (4.6).

5-(*N*-methylpyridinium-4-yl)-10,15,20-tris(4-dodecyloxyphenyl)porphyrin iodide (5a). 50 mg of **3a** (0.042 mmol) was dissolved in 40 mL of chloroform and 5 mL of DMF, 2 mL of methyl iodide was added to the solution of **3a**, and the mixture was then stirred under argon at room temperature overnight and monitored by TLC. After the end of the reaction, the solution was concentrated to about 3 mL and then 50 mL of ether was poured into the mixture. The precipitate was then filtered and washed with cold chloroform. The precipitate was further purified by column chromatography on silica gel with 10% CH_3OH in CH_2Cl_2. Yield: 55 mg, 98%. mp 181–182 °C. ^{1}H NMR ($CDCl_3$): δ, ppm 9.42 (d, 2H, *J* = 6 Hz, pyridyl-H), 8.89 (d, 2H, *J* = 6 Hz, pyridyl-H), 8.85 (d, 2H, *J* = 6 Hz, β-pyrrole-H), 8.78 (m, 4H, β-pyrrole-H), 8.63 (d, 2H, *J* = 6 Hz, β-pyrrole-H), 8.06 (d, 2H, *J* = 9 Hz, phenyl-H), 7.88 (d, 4H, *J* = 9 Hz, phenyl-H), 7.29 (d, 2H, *J* = 9 Hz, phenyl-H), 7.11 (d, 4H, *J* = 9 Hz, phenyl-H), 4.93 (s, 3H, N-*CH*$_3$), 4.26 (t, 2H, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 6.6 Hz, O-*CH*$_2$-), 4.11 (t, 4H, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 6.6 Hz, O-*CH*$_2$-), 2.01–1.91 (m, 6H, O-CH$_2$-*CH*$_2$-), 1.68–1.33 (m, 54H, -(CH$_2$)$_9$-), 0.94–0.89 (m, 9H, -*CH*$_3$), -2.74 (s, 2H). MS (MALDI-TOF): *m/z* 1182.72 [M - I]$^+$, 1182.81 calcd. for $C_{80}H_{104}N_5O_3$. UV-vis (CH_2Cl_2): λ_{max}, nm (ε × 10^{-3} $M^{-1}.cm^{-1}$) 422.0 (143), 522.0 (11), 584.0 (13), 663.0 (0.8). Anal. calcd. for $C_{80}H_{104}IN_5O_3$: C 73.31; H 8.00; N 5.34. Found: C 72.77; H 7.96; N 5.58.

5-(*N*-methylpyridinium-4-yl)-10,15,20-tris[3,4,5-tris(dodecyloxy)phenyl]porphyrin iodide (5b). To a solution of **3b** (0.022 mmol, 50 mg) dissolved in 40 mL chloroform and 5 mL of DMF was added 1.5 mL of methyl iodide slowly, and the mixture was then stirred under an argon atmosphere at room temperature overnight. The solvent was removed under reduced pressure. The solid residue was purified by column chromatography on a silica gel with 10% CH_3OH in $CHCl_3$. The product was recrystallized from $CHCl_3$/methanol mixture layered by hexane. Yield: 52 mg, 96%. Liquid. ^{1}H NMR ($CDCl_3$): δ, ppm 9.68 (d, 2H, *J* = 6.0 Hz, pyridyl-H), 9.13 (d, 2H, *J* = 6 Hz, pyridyl-H), 8.99 (m, 4H, β-pyrrole-H), 8.93 (t, 2H, *J* = 3 Hz, β-pyrrole-H), 8.84 (d, 2H, *J* = 6 Hz, β-pyrrole-H), 7.43 (s, 6H, phenyl-H), 5.10 (s, 3H, N-*CH*$_3$), 4.33 (t, 6H, *J* = 6 Hz, O-*CH*$_2$-), 4.12 (t, 12H, *J* = 6 Hz, O-*CH*$_2$-), 2.02-1.85 (m, 18H, O-CH$_2$-*CH*$_2$-), 1.70 (m, 6H, O-CH$_2$-CH$_2$-*CH*$_2$-), 1.49 (m, 12H, O-CH$_2$-CH$_2$-*CH*$_2$-), 1.32–1.23 (m, 144H, -(CH$_2$)$_8$-), 0.92–0.83 (m, 27H, -*CH*$_3$), -2.71 (s, 2H, NH). HR-MS (MALDI-TOF): *m/z* 2287.8661 [M - I]$^+$, 2287.9096 calcd. for $C_{152}H_{248}N_5O_9$. UV-vis (CH_2Cl_2): λ_{max}, nm (ε × 10^{-3} $M^{-1}.cm^{-1}$) 428.0 (122), 522.0 (12), 589.0 (1.1), 659.0 (0.6). Anal. calcd. for $C_{152}H_{248}IN_5O_9$: C 75.55; H 10.34; N 2.90. Found: C 75.90; H 10.30; N 2.85.

5-(*N*-methylpyridinium-4-yl)-10,15,20-tris(4-dodecyloxyphenyl)porphyrin tetrakis(pentafluorophenyl)-borate (6a). To a 3 mL CH_2Cl_2 solution of $NaB(C_6F_5)_4{\cdot}Et_2O$ (46.4 mg, 0.067 mmol) was added a 5 mL CH_2Cl_2 solution of **5a** (80 mg, 0.067 mmol). The reaction mixture was stirred for 48 h under argon before filtration to remove NaI. The filtrate was concentrated under reduced pressure to give a crude product, which was washed with heptane and sonicated for 1 h. The product was purified by recrystallization ($CHCl_3$/hexane). Any remaining volatile components were removed under reduced pressure to afford a purple-black solid. Yield: 101 mg, 80%. mp 128–129°C. ^{1}H NMR ($CDCl_3$): δ, ppm 8.98

(d, 2H, *J* = 6 Hz, pyridyl-H), 8.93–8.89 (m, 4H, pyridyl-H, β-pyrrole-H), 8.61 (d, 2H, *J* = 9 Hz, β-pyrrole-H), 8.51 (m, 4H, β-pyrrole-H), 8.08 (m, 6H, phenyl-H), 7.31 (m, 6H, phenyl-H), 4.44 (s, 3H, N-CH_3), 4.25 (m, 6H, O-CH_2-), 1.99 (m, 6H, O-CH_2-CH_2-), 1.64–1.28 (m, 54H, -$(CH_2)_9$-), 0.92 (m, 9H, -CH_3), -2.51 (s, 2H, NH). ^{19}F NMR ($CDCl_3$): δ, ppm -132.6 (d, 2F), -162.2 (t, 1F), -166.3 (t, 2F). MS (MALDI-TOF): *m/z* 1182.77 [M - $B(C_6F_5)_4$]$^+$, 1182.81 calcd. for $C_{80}H_{104}N_5O_3$. UV-vis (CH_2Cl_2): λ_{max}, nm (ε × 10^{-3} $M^{-1}.cm^{-1}$) 419.0 (131), 590.0 (1.6), 661.0 (1.1). Anal. calcd. for $C_{104}H_{104}BF_{20}N_5O_3$: C 67.06; H 5.63; N 3.76. Found: C 67.07; H 6.03; N 3.83.

5-(*N*-methylpyridinium-4-yl)-10,15,20-tris[3,4,5-tris(dodecyloxy)phenyl]porphyrin tetrakis(pentafluorophenyl)borate (6b). To a flask containing NaB-$(C_6F_5)_4Et_2O$ (25 mg, 0.035 mmol) was added a solution of **5b** (60 mg, 0.025 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 48 h under argon before filtration to remove NaI. The filtrate was diluted with CH_2Cl_2 and washed with brine, distilled water and dry over $MgSO_4$. The organic solution was concentrated under reduced pressure to give a crude product, which was purified by recrystallization ($CHCl_3$/methanol) to afford the oil porphyrin (51 mg, 69%). ^{1}H NMR ($CDCl_3$): δ, ppm 9.09 (d, 2H, *J* = 6 Hz, pyridyl-H), 8.99 (m, 4H, β-pyrrole-H), 8.85 (s, 4H, β-pyrrole-H), 8.59 (d, 2H, *J* = 6 Hz, pyridyl-H), 7.42 (s, 6H, phenyl-H), 4.65 (s, 3H, N-CH_3), 4.32 (t, 6H, *J* = 6 Hz, O-CH_2-), 4.10 (t, 12H, *J* = 6 Hz, O-CH_2-), 1.99 (m, 6H, O-CH_2-CH_2-), 1.87 (m, 12H, O-CH_2-CH_2-), 1.54–1.22 (m, 162H, -$(CH_2)_9$-), 0.91–0.83 (m, 27H, -CH_3), -2.59 (s, 2H, NH). ^{19}F NMR ($CDCl_3$): δ, ppm -132.6 (d, 2F), -162.2 (t, 1F), -166.3 (t, 2F). HR-MS (MALDI-TOF): *m/z* 2287.9025 [M - $B(C_6F_5)_4$]$^+$, 2287.9097 calcd. for $C_{152}H_{248}N_5O_9$. UV-vis (CH_2Cl_2): λ_{max}, nm (ε × 10^{-3} $M^{-1}.cm^{-1}$) 421.0 (113), 589.0 (14), 633.0 (0.8). Anal. calcd. for $C_{176}H_{248}BF_{20}N_5O_9$: C 71.21; H 8.42; N 2.36. Found: C 71.19; H 8.53; N 2.41.

5-(4-*N*-dodecanoylpyridinium-4-yl)-10,15,20-tris-[3,4,5-tris(dodecyloxy)phenyl]porphyrin bromide (7). Porphyrin **3b** (200 mg, 0.105 mmol) was added to 1.5 g (6 mmol) of 1-bromododecane in 100 mL of dry DMF and the mixture was then heated to reflux for 6 h under Ar. After evaporation of the solvent, the residual solid was washed with ether and filtered out. Purification of the solid by chromatography on silica gel with 10% CH_3OH-CH_2Cl_2 gave 217 mg product. Yield: 96%. mp 145–146 °C. ^{1}H NMR ($CDCl_3$): δ, ppm 9.78 (d, 2H, *J* = 6 Hz, pyridyl-H), 9.12 (d, 2H, *J* = 6 Hz, pyridyl-H), 8.99 (s, 4H, β-pyrrole-H), 8.85 (t, 4H, *J* = 6 Hz, β-pyrrole-H), 7.43 (s, 6H, phenyl-H), 5.37 (t, 2H, $^3J_{HH}$ = 6 Hz, $^3J_{HH}$ = 9 Hz, N-CH_2-), 4.32 (t, 6H, *J* = 6 Hz, O-CH_2-), 4.12 (t, 12H, *J* = 6 Hz, O-CH_2-), 2.40 (m, 2H, N-CH_2-CH_2-), 2.00 (m, 6H, O-CH_2-CH_2-), 1.91-1.87 (m, 12H, O-CH_2-CH_2-), 1.67-1.23 (m, 180H, -$(CH_2)_9$-), 0.93-0.83 (m, 30H, -CH_3), -2.70 (s, 2H, NH). MS (MALDI-TOF): *m/z* 2442.15 [M - Br]$^+$, 2442.08 calcd. for $C_{163}H_{270}N_5O_9$. UV-vis (CH_2Cl_2): λ_{max}, nm (ε × 10^{-3} $M^{-1}.cm^{-1}$) 427.0 (131), 524.0 (13), 593.0 (13), 659.0 (0.7). Anal. calcd. for $C_{163}H_{270}BrN_5O_9{\cdot}3H_2O$: C 76.77; H 10.29; N 2.65. Found: C 76.90; H 10.26; N 2.80.

5-(4-*N*-dodecanoylpyridinium-4-yl)-10,15,20-tris-[3,4,5-tris(dodecyloxy)phenyl]porphyrin tetrakis(pentafluorophenyl)borate (8). To a 3 mL CH_2Cl_2 solution of $NaB(C_6F_5)_4{\cdot}Et_2O$ (30.1 mg, 0.04 mmol) was added a 5 mL of CH_2Cl_2 solution of **7** (100 mg, 0.04 mmol). The reaction mixture was stirred for 48 h under argon. The solution was diluted with CH_2Cl_2. The organic solution was washed with distilled water, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The product was purified by recrystallization ($CHCl_3$/methanol) to afford an oily black product (104 mg, yield: 84%). Liquid. ^{1}H NMR ($CDCl_3$): δ, ppm 9.09 (d, 2H, *J* = 6 Hz, pyridyl-H), 8.99 (m, 4H, β-pyrrole-H), 8.90 (d, 2H, *J* = 9 Hz, β-pyrrole-H), 8.84 (d, 2H, *J* = 6.0 Hz, β-pyrrole-H), 8.62 (d, 2H, *J* = 3 Hz, pyridyl-H), 7.43 (s, 6H, phenyl-H), 4.78 (t, 2H, *J* = 6 Hz, N-CH_2-), 4.32 (t, 6H, *J* = 6.0 Hz, O-CH_2-), 4.10 (m, 12H, O-CH_2-), 2.31 (m, 2H, N-CH_2-CH_2-), 1.98 (m, 6H, O-CH_2-CH_2-), 1.90 (m, 12H, O-CH_2-CH_2-), 1.70–1.23 (m, 180H, -$(CH_2)_9$-), 0.92–0.84 (m, 30 H, -CH_3), -2.59 (s, 2H, NH). ^{19}F NMR ($CDCl_3$): δ, ppm -132.5 (t, 2F), -162.4 (m, 1F), -166.52 (m, 2F). MS (MALDI-TOF): *m/z* 2442.00 [M - $B(C_6F_5)_4$]$^+$, 2442.08 calcd. for $C_{163}H_{270}N_5O_9$. UV-vis (CH_2Cl_2): λ_{max}, nm (ε × 10^{-3} $M^{-1}.cm^{-1}$) 423.0 (118), 593.0 (15), 664.0 (0.9). Anal. calcd. for $C_{163}H_{270}BF_{20}N_5O_9$: C 71.92; H 8.71; N 2.24. Found: C 72.14; H 8.82; N 2.35.

5,15-di(*N*-methylpyridinium-4-yl)-10,20-bis(4-dodecyloxyphenyl)porphyrin diiodide (9a). To a solution of **4a** (50 mg, 0.05 mmol) dissolved in 45 mL of chloroform and 5 mL of DMF was added 2 mL of methyl iodide, and the reaction mixture was stirred under argon at room temperature for two days and monitored by TLC. The solution was then concentrated to about 3 mL and then 50 mL of ether was poured into the mixture. The precipitate was then filtered and washed with chloroform. After drying of the precipitate under vacuum, it was recrystallized from mixed solvents of chloroform and methanol with layered hexane. Yield: 61 mg, 96%. mp 235–236 °C. ^{1}H NMR (DMSO-d_6): δ, ppm 9.47 (d, 4H, *J* = 6 Hz, pyridyl-H), 9.01 (d, 12H, *J* = 6 Hz, pyridyl-H and β-pyrrole-H), 8.12 (d, 4H, *J* = 9 Hz, phenyl-H), 7.41 (d, 4H, *J* = 9 Hz, phenyl-H), 4.72 (s, 6H, N-CH_3), 4.27 (t, 4H, *J* = 6 Hz, OCH_2-), 1.91 (m, 4H, OCH$_2$-CH_2-), 1.57 (m, 4H, OCH$_2$-CH$_2$-CH_2-), 1.47–1.21 (m, 32H, -$(CH_2)_8$-), 0.86 (m, 6H, -CH_3), -2.94 (s, 2H, NH). MS (MALDI-TOF): *m/z* 1015.62 [M - 2I + H]$^+$, 1015.66 calcd. for $C_{68}H_{83}N_6O_2$. UV-vis (CH_2Cl_2): λ_{max}, nm (ε × 10^{-3} $M^{-1}.cm^{-1}$) 438.0 (115), 526.0 (9.4), 574.0 (11), 666.0 (7.5). Anal. calcd. for $C_{68}H_{82}I_2N_6O_2{\cdot}4H_2O$: C 60.89; H 6.76; N 6.27. Found: C 60.89; H 6.36; N 6.46.

5,15-di(*N*-methylpyridinium-4-yl)-10,20-bis[3,4,5-tris(dodecyloxy)phenyl]porphyrin diiodide (9b). To 100 mg of 5,15-dipyridyl-10,20-bis(3,4,5-tris(dodecyloxy)phenyl)porphyrin (0.058 mmol) dissolved in 45 mL

of chloroform and 5 mL of DMF was slowly added 2.0 mL of methyl iodide, and the mixture was then stirred under an argon atmosphere at room temperature overnight. The solvent was removed under reduced pressure. The solid residue was purified by column chromatography on a silica gel using 10% CH_3OH-$CHCl_3$ as eluent. The product was recrystallized from $CHCl_3$/methanol/hexane. Yield: 96% (111 mg). mp 181–183 °C. ^{1}H NMR ($CDCl_3$): δ, ppm 9.66 (d, 4H, *J* = 6 Hz, pyridyl-H), 9.12 (d, 4H, *J* = 3 Hz, pyridyl-H), 9.00 (s, 4H, β-pyrrole-H), 8.77 (d, 4H, *J* = 6.0 Hz, β-pyrrole-H), 7.38 (s, 4H, phenyl-H), 5.08 (s, 6H, N-*CH*$_3$), 4.32 (t, 4H, *J* = 6 Hz, O-*CH*$_2$-), 4.11 (t, 8H, *J* = 6 Hz, O-*CH*$_2$-), 2.01 (m, 4H, O-CH$_2$-*CH*$_2$-), 1.90 (m, 8H, O-CH$_2$-*CH*$_2$-), 1.72–1.20 (m, 108H, -(*CH*$_2$)$_9$-), 0.91-0.80 (m, 18H, -*CH*$_3$), -3.15 (s, 2H, NH). HR-MS (MALDI-TOF): *m/z* 1752.3856 [M - 2I + H]$^+$, 1752.3881 calcd. for $C_{116}H_{179}N_6O_6$. UV-vis (CH_2Cl_2): λ_{max}, nm (ε × 10^{-3} $M^{-1}.cm^{-1}$) 441.0 (220), 526.0 (17.9), 575.1 (18.1), 663.0 (11.1). Anal. calcd. for $C_{116}H_{178}I_2N_6O_6$: C 69.44; H 8.94; N 4.19. Found: C 69.46; H 8.75; N 4.26.

5,15-di(*N*-methylpyridinium4-yl)-10,20-bis[3,4,5-tris(dodecyloxy)phenyl]porphyrin di-[tetrakis(pentafluorophenyl)borate] (10). To a 3 mL CH_2Cl_2 solution of $NaB(C_6F_5)_4{\cdot}Et_2O$ (70 mg, 0.1 mmol) was added a 5 mL CH_2Cl_2 solution of **9b** (100 mg, 0.05 mmol*)*. The reaction mixture was stirred for 48 h under argon before filtration to remove NaI. The filtrate was diluted with CH_2Cl_2 then washed with distilled water two times. The organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and the solid product was purified by recrystallization ($CHCl_3$/methanol). Any remaining volatile components were removed under reduced pressure to afford a violet-black solid. Yield: 122 mg (78%). mp 65–66 °C. ^{1}H NMR ($CDCl_3$): δ, ppm 9.32 (d, 4H, *J* = 6.0 Hz, pyridyl-H), 9.12 (d, 4H, *J* = 6 Hz, pyridyl-H), 8.85 (d, 4H, *J* = 6.0 Hz, β-pyrrole-H), 8.76 (d, 4H, *J* = 3 Hz, β-pyrrole-H), 7.41 (s, 4H, phenyl-H), 4.89 (s, 6H, N-*CH*$_3$), 4.32 (t, 4H, *J* = 6 Hz, O-*CH*$_2$-), 4.07 (t, 8H, *J* = 6 Hz, O-*CH*$_2$-), 2.01 (m, 4H, O-CH$_2$-*CH*$_2$-), 1.80 (m, 8H, O-CH$_2$-*CH*$_2$-), 1.76–1.18 (m, 108H, -(*CH*$_2$)$_9$-), 0.84 (m, 18H, -*CH*$_3$), -2.72 (s, 2H, NH). ^{19}F NMR ($CDCl_3$): δ, ppm -132.7 (d, 2F), -162.3 (m, 1F), -166.5 (m, 2F). HR-MS (MALDI-TOF): *m/z* 1752.3809 [M - 2B$(C_6F_5)_4$ + H]$^+$, 1752.3881 calcd. for $C_{116}H_{179}N_6O_6$. UV-vis (CH_2Cl_2): λ_{max}, nm (ε × 10^{-3} $M^{-1}.cm^{-1}$) 445.0 (153.3), 526.0 (11.9), 581.0 (16.1), 668.0 (10.1). Anal. calcd. for $C_{164}H_{178}B_2F_{40}N_6O_6$: C 63.32; H 5.77; N 2.70. Found: C 64.88; H 6.90; N 3.25.

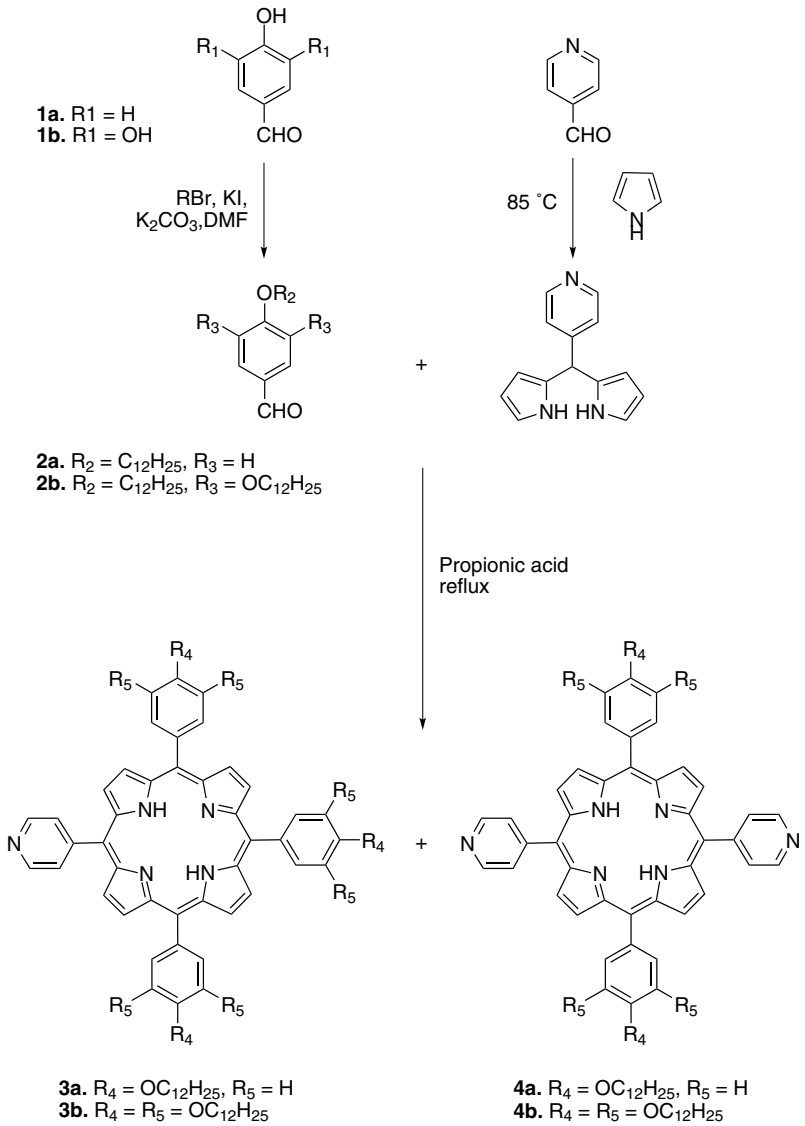
5,15-di-(4-*N*-dodecanoylpyridinium-4-yl)-10,20-bis[3,4,5-tris(dodecyloxy)phenyl]porphyrin dibromide (11). Porphyrin **4b** (200 mg, 0.116 mmol) was added to 2.0 g (8 mmol) of 1-bromododecane in 100 mL of dry DMF and the mixture was then heated to reflux for 6 h. After evaporation of the solvent, the residual solid was washed with ether and filtered out. Purification of the solid by chromatography on silica gel with 10% CH_3OH-CH_2Cl_2 gave the title product in 97% yield (250 mg). mp 177–179 °C. ^{1}H NMR ($CDCl_3$): δ, ppm 9.82 (d, 4H, *J* = 6 Hz, pyridyl-H), 9.03 (d, 4H, *J* = 6 Hz, pyridyl-H), 8.85 (s, 4H, β-pyrrole-H), 8.63 (d, 4H, *J* = 3 Hz, β-pyrrole-H), 7.32 (s, 4H, phenyl-H), 5.34 (t, 4H, $^3J_{HH}$ = 9 Hz, $^3J_{HH}$ = 6 Hz, N-*CH*$_2$-), 4.32 (t, 4H, *J* = 6 Hz, O-CH$_2$-), 4.09 (t, 8H, $^3J_{HH}$ = 6 Hz, $^3J_{HH}$ = 9 Hz, O-CH$_2$-), 2.39 (m, 4H, N-CH$_2$-*CH*$_2$-), 1.88 (m, 4H, O-CH$_2$-*CH*$_2$-), 1.75 (m, 8H, O-CH$_2$-*CH*$_2$-), 1.53–1.22 (m, 144H, -(*CH*$_2$)$_9$-), 0.85 (m, 24H, -*CH*$_3$), -3.55 (s, 2H, NH). MS (MALDI-TOF): *m/z* 2060.76 [M - 2Br + H]$^+$, 2060.73 calcd. for $C_{138}H_{223}N_6O_6$. UV-vis (CH_2Cl_2): λ_{max}, nm (ε × 10^{-3} $M^{-1}.cm^{-1}$) 435.0 (166), 526 (12), 575.0 (12), 663.0 (7.7). Anal. calcd. for $C_{138}H_{222}Br_2N_6O_6$: C 74.62; H 10.07; N 3.78. Found: C 74.21; H 9.73; N 3.91.

5,15-di-(4-*N*-dodecanoylpyridinium-4-yl)-10,20-bis[3,4,5-tris(dodecyloxy)phenyl]porphyrin di-[tetrakis(pentafluorophenyl)borate] (12). To a 3 mL CH_2Cl_2 solution of $NaB(C_6F_5)_4{\cdot}Et_2O$ (68.4 mg, 0.097 mmol) was added a 5 mL of CH_2Cl_2 solution of **11** (100 mg, 0.045 mmol). The reaction mixture was stirred overnight. The resulting solution was diluted with CH_2Cl_2 and washed with brine, distilled water and then dried over $MgSO_4$. The organic solvent was removed under reduced pressure. The product was purified by recrystallization from $CHCl_3$/methanol. Any remaining volatile components were removed under reduced pressure to afford the violet-black solid (134 mg, yield: 87%). mp 98–100 °C. ^{1}H NMR ($CDCl_3$): δ, ppm 9.06 (d, 4H, *J* = 6 Hz, pyridyl-H), 8.97 (d, 4H, *J* = 6 Hz, β-pyrrole-H), 8.85 (d, 4H, *J* = 6 Hz, β-pyrrole-H), 8.56 (d, 4H, *J* = 6 Hz, pyridyl-H), 7.38 (s, 4H, phenyl-H), 4.80 (t, 4H, $^3J_{HH}$ = 9 Hz, $^3J_{HH}$ = 6 Hz, N-*CH*$_2$-), 4.27 (t, 4H, $^3J_{HH}$ = 9 Hz, $^3J_{HH}$ = 6 Hz, O-*CH*$_2$-), 3.96 (t, 8H, *J* = 6 Hz, O-*CH*$_2$-), 2.31 (m, 4H, N-CH$_2$-*CH*$_2$-), 1.96 (m, 4H, O-CH$_2$-*CH*$_2$-), 1.67 (m, 16H, O-CH$_2$-*CH*$_2$-), 1.50–1.18 (m, 136H, -(CH$_2$)$_9$-), 0.88 (m, 24H, -CH$_3$), -2.66 (s, 2H, NH). ^{19}F NMR ($CDCl_3$): δ, ppm -132.6 (d, 2F), -162.2 (t, 1F), -166.3 (t, 2F). MS (MALDI-TOF): *m/z* 2060.59 [M -2B$(C_6F_5)_4$ + H]$^+$, 2060.73 calcd. for $C_{138}H_{223}N_6O_6$. UV-vis (CH_2Cl_2): λ_{max}, nm (ε × 10^{-3} $M^{-1}.cm^{-1}$) 453.0 (153), 527.0 (12.7), 583.0 (19.4), 668.0 (12.7). Anal. calcd. for $C_{186}H_{222}B_2F_{40}N_6O_6$: C 65.33; H 6.54; N 2.46. Found: C 65.33; H 6.58; N 2.53.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthetic approach in order to access to free base porphyrin precursors **3a**–**4b** is shown in Scheme 1. 4-(dodecyloxy)benzaldehyde and 3,4,5-tris(dodecyloxy)-benzaldehyde were prepared according to the literature [40, 41]. The free-base porphyrins (**3a**, **3b**, **4a**, **4b**) were successfully synthesized from the propionic acid-catalyzed condensation of 5-(4-pyridyl)dipyrromethane [42] with the corresponding aldehyde under reflux in the dark for 2.5 h. The solvent was removed under reduced

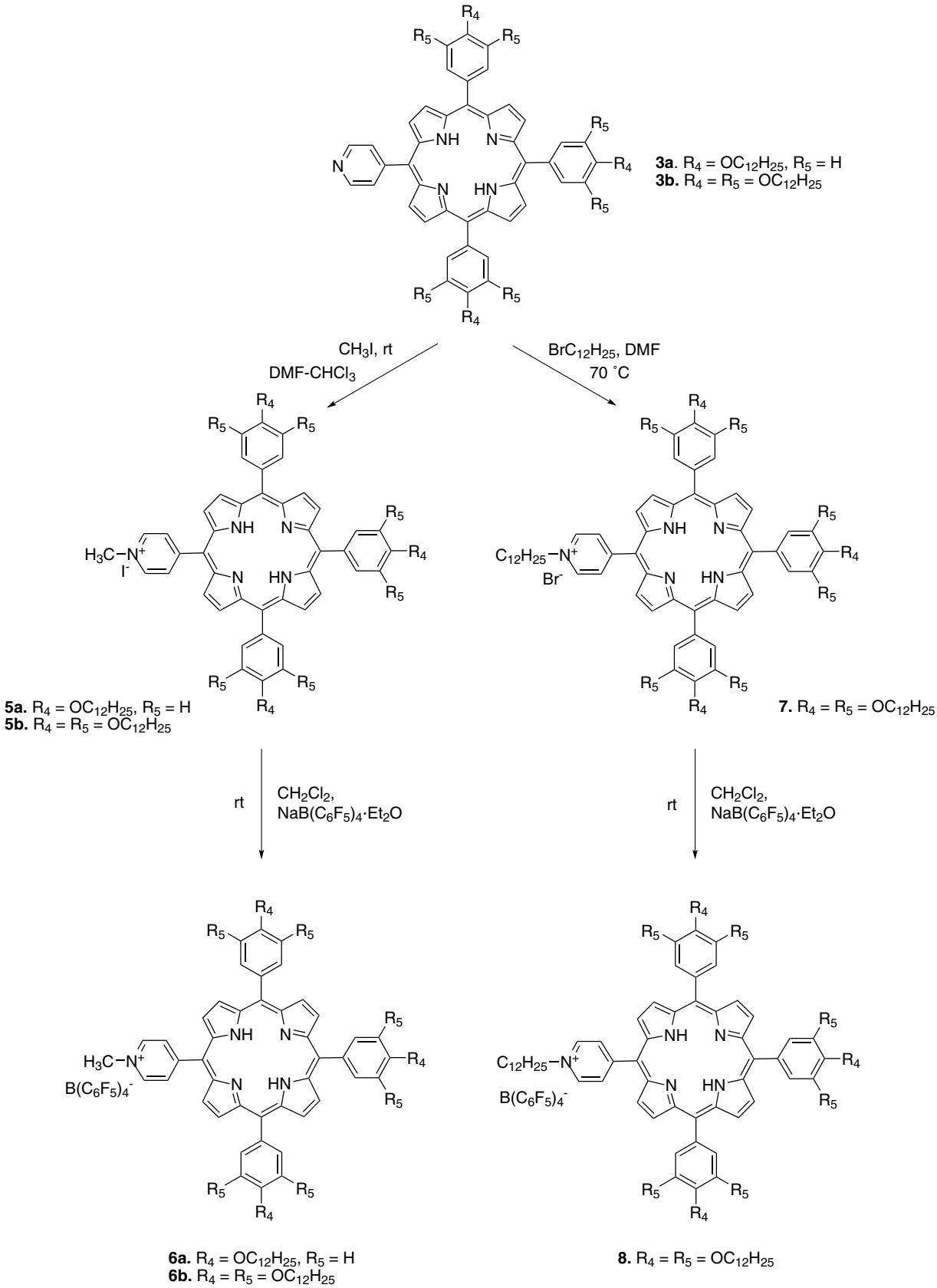


Scheme 1. Synthetic scheme of porphyrins **3** and **4**

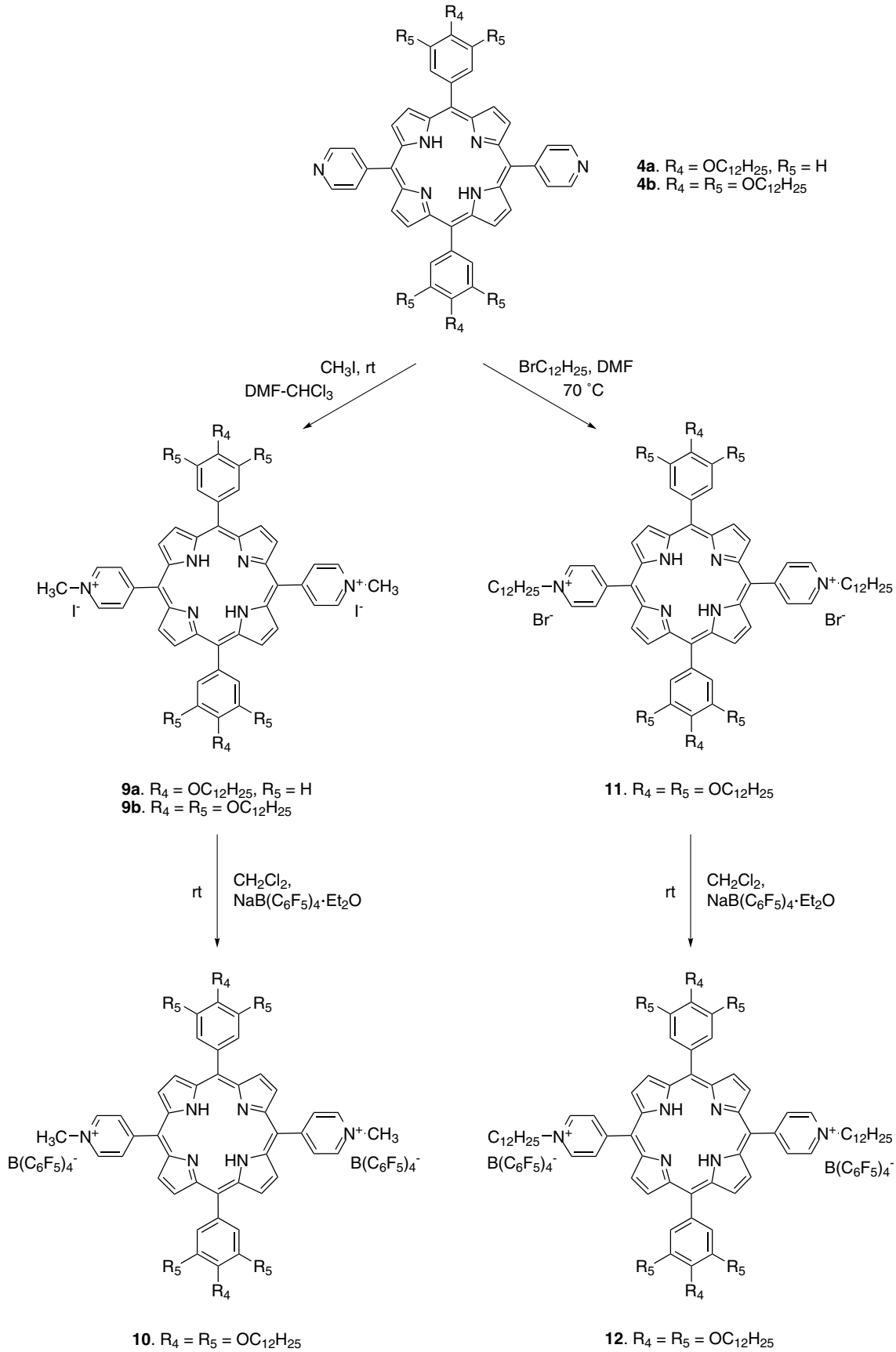
pressure and the residues were purified by column chromatography on silica gel by using a 0–5% CH_3OH in CH_2Cl_2 mixture as the eluent. Recrystallization of the resulting solid with $CHCl_3/CH_3OH$, afforded the corresponding porphyrins **3** and **4** in 8–15% yields. Several different condensation conditions were also explored in order to optimize the reaction conditions leading to compounds **3** and **4**. Trifluoroacetic acid (TFA) or boron trifluoride etherate as catalysts in chloroform or dichloromethane at room temperature were not suitable for any of the present reactions: no expected porphyrin derivative could be obtained from the reactions in the presence of these two catalysts. All these new porphyrin compounds were characterized by ^{1}H NMR, UV-vis spectroscopy and MALDI-TOF mass spectrometry.

The ^{1}H NMR spectrum of the porphyrin **4b** is shown in Fig. 1a as a representative example. The porphyrin **4b** displays resonances peaks at 8.83, 8.18 and -2.81 ppm, which are assigned to the β-pyrrole and NH protons respectively. The phenyl and pyridyl *meso* substituents of the free-base porphyrin have signals located at 7.45 and 9.04 ppm, respectively. In the aliphatic area, relative to the long alkyl chains, two triplet signals at 4.33 (4H) and 4.12 (8H) ppm are respectively accounting for the methylene protons (α-CH_2) 1′ and 1 linked to the oxygen atoms. The resonances of the β-methylene protons 2′ and 2 appear as muliplets at 2.01 (4H) and 1.90 (8H) ppm, respectively. The methyl protons have signals located between 0.85–0.95 ppm. Other protons of the alkyl chains are less well resolved with resonances in the region 1.25–1.70 ppm. **3a**, **3b** and **4a** exhibit similar proton NMR spectra as for **4b**. The low-field signals (7.29–9.07 ppm) correspond to the protons of the pyridyl groups, β-pyrrole and phenyl groups. The high-field signals (singlet at about -2.80 ppm, 2H) are assigned to the NH protons. The resonances for the α-methylene and β-methylene protons appear at around 4.11 and 2.01 ppm as triplets, respectively. The resonances of the remaining protons of the methylene and methyl groups are located between 0.91 and 2.06 ppm. ^{1}H NMR data of these derivatives are given in the Experimental Section and spectra are shown in the Supporting information.

The synthetic routes used for the preparation of the ionic porphyrin derivatives are shown in Schemes 2 and 3. The bromide salts (**7** and **11**) were synthesized by reaction of 1-bromododecane with the corresponding neutral porphyrin in DMF at 70 °C followed by purification by column chromatography and recrystallization in nearly quantitative yields. Similarly, compounds **3** and **4** were methylated in a dimethylformamide/chloroform mixture under reflux by using CH_3I to afford compounds **5** and **9** in 97% yield (Schemes 2 and 3). Tetrakis(perfluorophenyl)-borate salts were prepared by anionic exchange of bromide or iodide porphyrins with a little excess of sodium tetrakis(perfluorophenyl)borate ($NaB(C_6F_5)_4$) in dichloromethane at room temperature. The insoluble, inorganic salts, NaBr and NaI, were removed by filtration under vacuum and the organic solutions were washed with distilled water. The porphyrin salts were finally isolated in relatively high yields (69–87%). However, the reaction of **9a** with sodium tetrakis(perfluorophenyl)borate was not successful using the similar synthetic method described for **9b**, probably due to the poor solubility of the precursor **9a** in the organic solvent. All these porphyrin salts



Scheme 2. Synthetic scheme of cationic porphyrins **5a**–**8**



Scheme 3. Synthetic scheme of cationic porphyrins **9a**–**12**

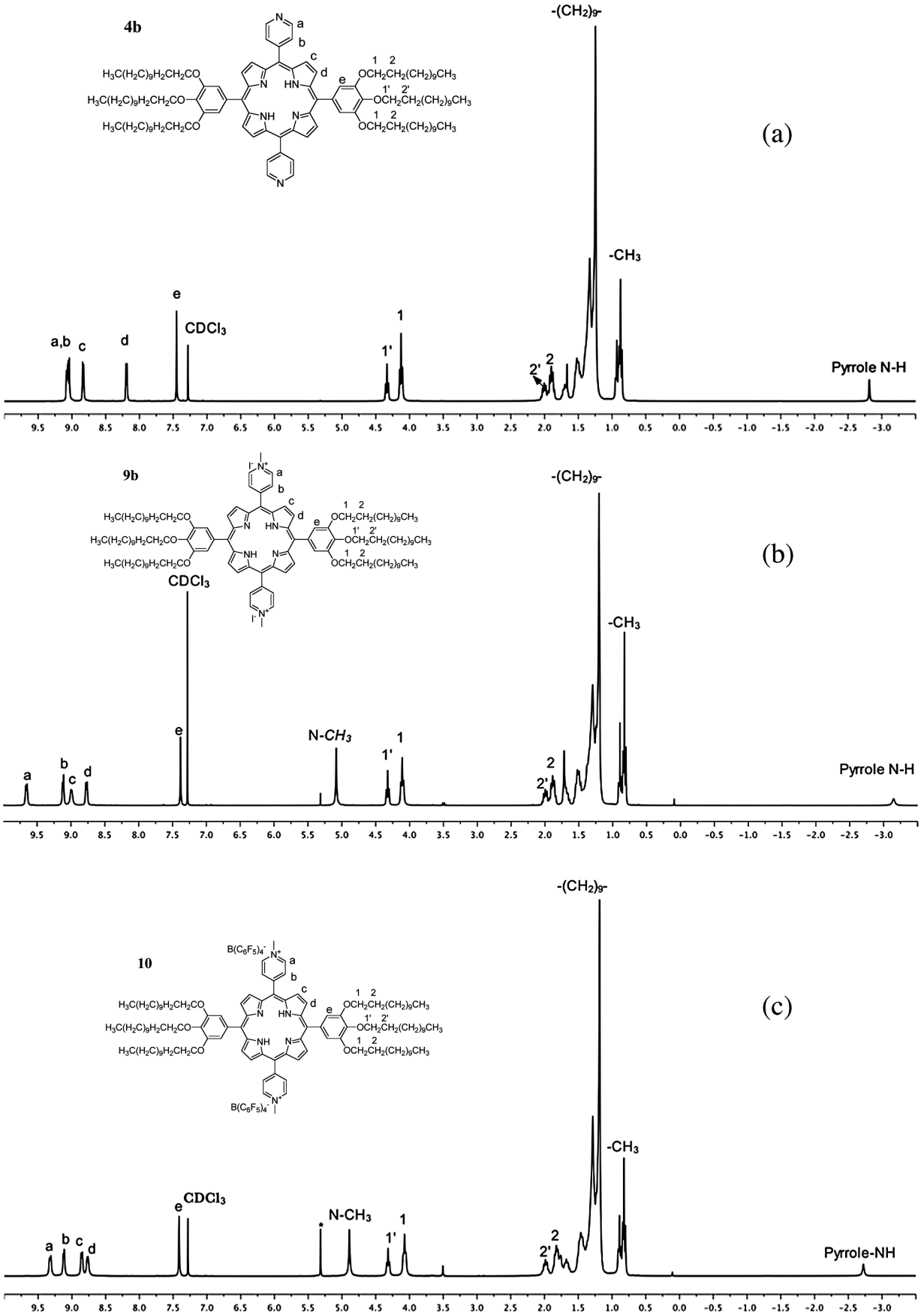


Fig. 1. Representative 300 MHz ^{1}H NMR spectra of porphyrins **4b** (a), **9b** (b) and **10** (c) in $CDCl_3$ (*solvent: CH_2Cl_2)

are very immiscible with water and the hydrophobicity of these compounds can be attributed to the high water-repellency of the long alkyl chains of the cationic part of the molecule and the low polarizability. This property facilitated purification by simply washing the crude product with distilled water in order to remove any traces of water soluble impurities.

Some of the porphyrin salts that have been prepared are solid with exception of compounds **5b**, **6a**, and **8** which are liquid at room temperature. All the structures and compositions of these new porphyrin salts were determined by ^{1}H and ^{19}F NMR spectroscopy, MALDI-TOF mass spectrometry (MS and HRMS), UV-visible spectroscopy and elemental analysis. MALDI-TOF mass spectrometry technique was used firstly to characterize these porphyrin compounds and their salts. All the studied compounds exhibit one main peak (protonated molecule for neutral derivatives or cationic part of the molecule for ionic liquids). These data confirmed the expected structures. For example, the MALDI-TOF mass spectrum of **8** exhibits the parent-ion peak at *m/z* = 2442.00 for cationic part (calculated for $C_{163}H_{270}N_5O_9$ *m/z* = 2442.08) (Fig. 2).

The well-resolved proton NMR spectra of **5a**, **5b**, **7**, **9a**, **9b** and **11**, shown in the Supporting information are very well consistent with the expected structures and exhibit similar chemical shifts. The proton resonances occur in four distinct regions. The downfield region from 7 to *ca*. 10 ppm correspond to pyridine ring protons (*ca*. 9.80 and 9.03 ppm for **7** and **11**, *ca*. 9.67 and 9.12 ppm for **5b** and **9b**, *ca*. 9.44 and 9.00 ppm for **5a** and **9a**), β-pyrrolic protons (*ca*. 9.00 and 8.70 ppm for **7**, **11**, **5b** and **9b**; 8.86 and 8.63 ppm for **5a**, 9.01 ppm for **9a**) and phenyl protons (*ca*. 7.30 ppm for **9b** and **11** as singlets, 7.43 ppm for **5b** and **7** as singlets, 7.09–8.08 ppm for **5a** as doublets, 8.11 and 7.40 ppm for **9a** as doublets). The medium range resonances (between 4 and 6 ppm) are respectively attributed to –O-CH_2-protons (4.27 ppm for **9a**; 4.26 and 4.11 ppm for **5a**; 4.33 and 4.12 ppm for **5b**, **7**, **9b** and **11**), N-CH_2-protons (5.37 ppm for **7**; 5.34 ppm for **11**) and N-CH_3 protons (*ca*. 5.10 ppm for **5b** and **9b**; 4.93 ppm for **5a**; 4.72 ppm for **9a**). Higher field resonances (between 0.5 and 2.5 ppm) are attributed to the remaining aliphatic protons. The last region near -3.0 ppm corresponds to inner NH proton resonances (-2.70 ppm for **5b** and **7**; -2.74 ppm for **5a**; -2.94 ppm for **9a**; -3.62 ppm for **11**; -3.15 ppm for **9b**). By comparison of the proton NMR spectra of the ionic porphyrins with that of the corresponding neutral ones, the alkylated pyridyl rings do not induce significant shifts on proton resonances with the exception of the pyridine α protons which demonstrate a downfield shift. As an example, the ^{1}H NMR spectrum of **9b** is given on Fig. 1b. For **9b**, pyridine α protons are shifted to 9.66 pm (9.04 ppm for **4b**) while pyridine α protons resonances remain almost unchanged (see Fig. 1a for comparison).

The completion of the anionic exchange reaction of bromide or iodide with tetrakis(perfluorophenyl)borate was confirmed by mass spectrometry, ^{1}H NMR and ^{19}F NMR. In the negative mode MALDI/TOF mass spectra of these derivatives, a single ionic pattern a *m/z* = 679 corresponding to the $B(C_6F_5)_4^-$ ion was detected. In contrast to the precursors, remarkable changes in the proton NMR spectra take place in the pyridinium α protons, the

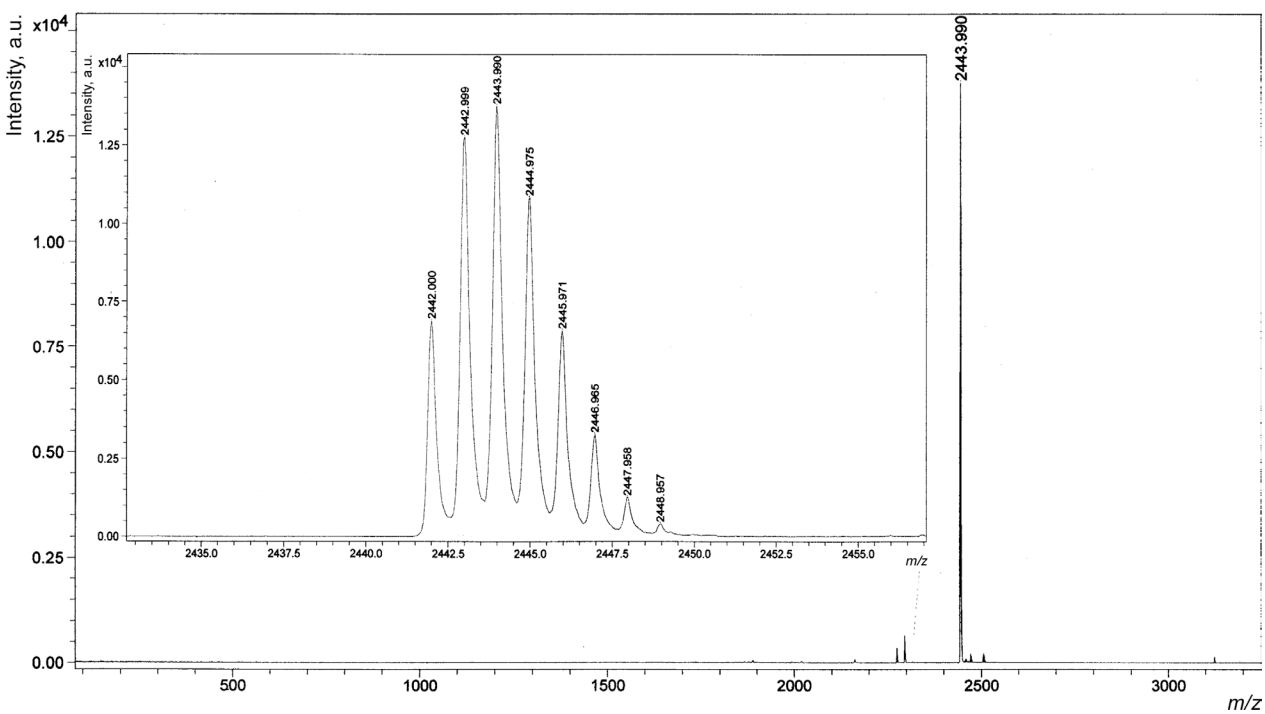


Fig. 2. MALDI-TOF mass spectrum of **8** (cationic part)

methylene or the methyl groups adjacent to *N*-pyridyl (*N*-CH_2-) or (*N*-CH_3) which are shifted to higher field due to the influence of the large $B(C_6F_5)_4^-$ anion. The remaining proton resonances do not exhibit change with respect to the precursors. As an example, the ^1H NMR spectrum of **10** is given in Fig. 1c. When compared to the spectrum of **9b** (Fig. 1b), the pyridinium α and N-CH_3 protons of **10** appear at 9.32 and 4.32 ppm, respectively (9.66 and 5.08 ppm for **9b** respectively). In addition, the resonances of the inner NH protons in **10** are shifted to lower field (-2.72 ppm compared to **9b** (-3.15 ppm)). The ^{19}F NMR spectra (given in Supporting information) of **6a**, **6b**, **8a**, **10** and **12** also confirmed the presence of $B(C_6F_5)_4^-$ ion. The resonances of the *para*-, *ortho*- and *meta*-fluorine atoms appear at -162.2, -132.6 and -166.3 ppm respectively.

The UV-vis data of the neutral porphyrins and the porphyrin salts are given in Table 1. The UV-vis spectra of **4b**, **9b** and **10** in CH_2Cl_2 are presented in Fig. 3. The neutral porphyrin **4b** shows a typical electronic spectrum of *meso*-substituted porphyrins in CH_2Cl_2 with a sharp Soret band at 421 nm and four Q-bands at 519, 550, 591 and 646 nm. Upon cationization of the neutral porphyrin **4b**, the number of absorption bands in **9b** and **10** is reduced. Three Q-bands appear at 526 (526), 575 (581) and 663 (668) nm for **9b** (**10**). The most relevant feature is the red-shift of the Soret band upon alkylation of the pyridyl groups. For example, the Soret band of the *N*-methylated porphyrin **9b** is red-shifted by 20 nm from the corresponding Soret bands of **4b**. When I^- is substituted by $B(C_6F_5)_4^-$, the Soret band of **10** is further red-shifted to 445 nm (see Fig. 3). Similar trend is observed for other derivatives (Table 1). Another interesting feature can be observed on the UV-vis spectra. The Soret bands of the porphyrin salts are significantly broadened and their extinction coefficients are remarkably decreased relative to those of the corresponding neutral porphyrins (Fig. 3 and Table 1).

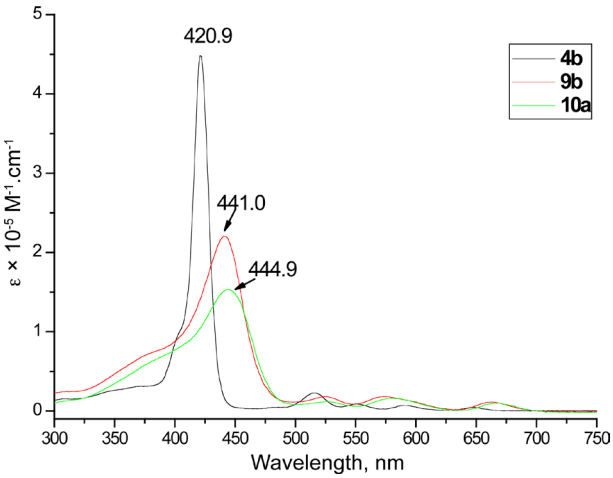


Fig. 3. UV-vis spectrum (CH_2Cl_2) of porphyrins **4b, 9b** and **10**

TGA measurements

TGA analyses were performed under a Ar/O_2 gas stream mixture for six porphyrins in order to correlate their thermal stability to their structure (Fig. 4). The less stable structures are porphyrins **9b** and **5a** since their decomposition began at 183 °C and 193 °C respectively and a further mass decrease occurred starting from 370 °C due to the porphyrin calcination. TGA curves indicated a first 13.5% weight loss for **9b** and 11.3% for **5a** assigned to methyl iodide release during the heating

Table 1. UV-vis absorption data in CH_2Cl_2 for the synthesized derivatives

Compound	λ_{max}, nm ($\varepsilon \times 10^{-3}$, $M^{-1}.cm^{-1}$)				
	Soret band		Q-bands		
3a	421 (1769)	517 (71)	555 (46)	592 (26)	650 (27)
3b	421 (350)	516 (18)	552 (8.7)	591 (4.8)	649 (4.2)
4a	420 (1622)	515 (72)	552 (37)	591 (23)	650 (18)
4b	421 (449)	516 (22.7)	550 (8.8)	591 (7.0)	646 (4.6)
5a	422 (143)	522 (11)	584 (13)	663 (0.8)	
5b	428 (122)	522 (12)	589 (1.1)	659 (0.6)	
6a	419 (131)	590 (1.6)	661 (1.1)		
6b	421 (113)	589 (14)	633 (0.8)		
7	427 (131)	524 (13)	593 (13)	659 (0.7)	
8	423 (118)	593 (15)	664 (0.9)		
9a	438 (115)	526 (9.4)	574 (11)	666 (7.5)	
9b	441 (220)	526 (17.9)	575 (18.1)	663 (11.1)	
10	445 (153)	526 (11.9)	581 (16.1)	668 (10.1)	
11	435 (166)	526 (12)	575 (12)	663 (7.7)	
12	453 (153)	527 (12.7)	581 (19.4)	668 (12.7)	

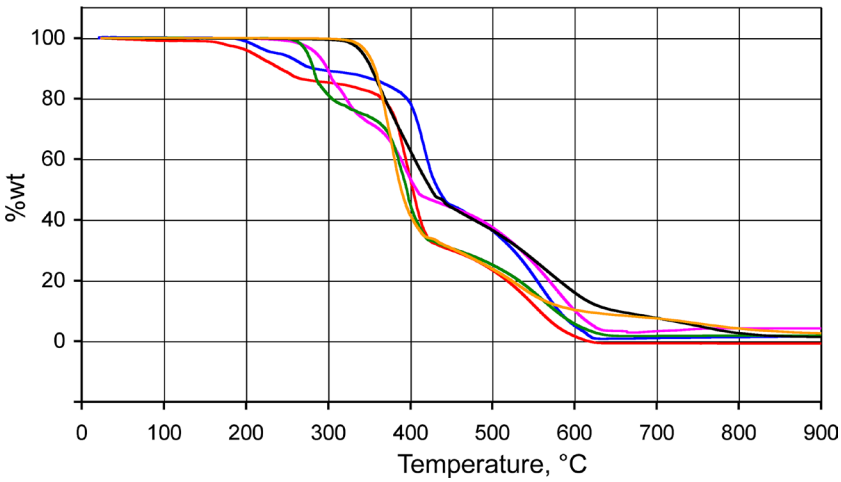


Fig. 4. TGA traces for porphyrins **5a** (blue line), **6a** (black line), **9a** (pink line), **9b** (red line), **11** (green line) and **12** (orange line) under an Ar/O_2 gas stream (30 $mL.min^{-1}$/10 $mL.min^{-1}$)

process. The respective theoretical values are 14.1% and 10.8%. This result demonstrates that when iodide is used as the counter-anion, the thermal stability is quite low compared to porphyrins **11**, **12** and **6a** with other counter-anions. Compound **9a** is surprisingly more stable than **9b** and **5a** despite the presence of two iodide ions and this is may be due to electronic effects since **9a** possess less donor atoms and is then less oxidizable. Nevertheless, a straightforward correlation was observed between the thermal stability and the nature of the counter-anion if we compared **11** *vs.* **12**, **5a** *vs.* **6a** and **9b** *vs.* **11**. From this result, a stability series clearly emerged: $I^- < Br^- << B(C_6F_5)_4^-$. Moreover, if we compare **6a** and **12**, the number and the length of the peripheral alkyl chains seem to have no effect on the thermal stability of the porphyrins.

Phase transition

The thermal properties and solid-liquid phase transitions of these porphyrin salts were examined by differential scanning calorimetry (DSC) upon heating and cooling down (heating and cooling rate: 10 °C. min^{-1}). Endothermic or exothermic peaks assigned as the melting or crystallizing processes were observed below 300 °C. The measured data of glass transition temperature (Tg), solid-solid transition (Ts-s), and melting point (Tm) are presented in Table 2. Porphyrin **9a** has a melting point at 236 °C. **5a**, **6a**, **7** and **9b** have melting points below 200 °C, while **5b**, **6b**, **8**, **10** and **12** have melting temperatures ranging from 98 to 181 °C. More interesting is the behavior of **5b**, **6b**, and **8** salts which can be considered as room-temperature ionic liquids due to low melting points observed below 25 °C. To our knowledge, these are the first examples of porphyrins displaying ionic liquid properties close to room temperature.

The first type of behavior is characterized by the salts that have a melting transition (**6a**, **6b**, **7**, **9b**, **10**, **11** and **12** in Table 1). The second type of behavior is represented by a number of salts that exhibited one solid-solid

Table 2. Thermal and conductivity properties of the ionic liquid salts

Compound	Tg, °C[a]	Ts-s, °C[b]	Tm, °C[c]	ΔHm, $kJ.mol^{-1}$	ΔSm, $J.mol^{-1}.K^{-1}$ [d]	κ/$mS.cm^{-1}$ [e]
5a		91	181	26.61	58.09	solid
5b	-28					1.32
6a			129	67.30	163.35	solid
6b			-23	8.53	34.13	4.01
7			145	17.99	42.75	solid
8		-39	-22	1.28	5.12	0.05
9a		213	236	27.86	54.00	solid
9b			181	37.18	81.89	solid
10			66	21.43	49.72	solid
11			177	31.73	70.52	solid
12			98	88.35	236.24	solid

[a] Glass transition. [b] Solid-solid transition. [c] Melting point. [d] Entropy of fusion (ΔSm = ΔHm/Tm, where ΔHm is melting enthalpy at Tm(K)). [e] Specific conductivity at 22 °C.

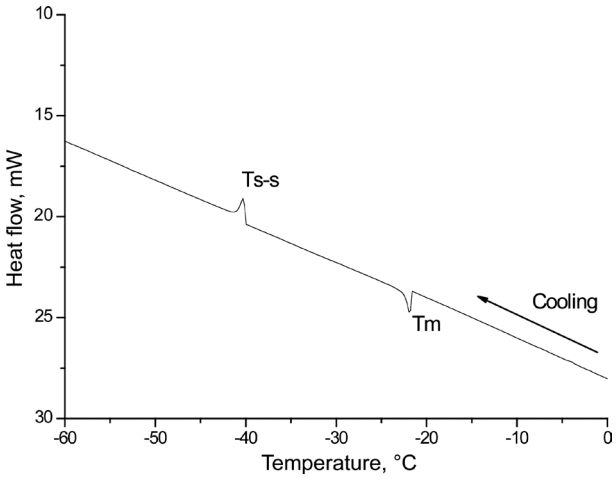


Fig. 5. DSC traces on second cooling for porphyrin **8**

transition (Ts-s) before melting (compounds **5a**, **8** and **9a**). The third type of behavior is represented by the salt that only exhibited a glass transition at 200 °C without melting (**5b**). Figure 5 shows the DSC traces of one of the representatives, porphyrin (**8**) as an example, Upon cooling, **8** undergoes a single liquid-solid phase transition at approximately T = -22 °C, showing an exothermic peak and exhibit afterwards a solid-solid phase transition at -39 °C with an endothermic peak.

A comparison of the melting point values of the asymmetric porphyrin based salts with those of the symmetric porphyrin based ones clearly evidences the influence of the asymmetry on the melting temperature. The melting point values of the asymmetric porphyrin salts (mono-alkylated) are lower than those for the corresponding symmetric salts (di-alkylated). For the same anion, the salts with lower symmetry porphyrins generally exhibit a lower melting point than those with higher symmetry (see Table 2, **5a** *vs.* **9a**, **5b** *vs.* **9b**, **7** *vs.* **11**, **6b** *vs.* **10**, **8** *vs.* **12**). These results suggest that the packing efficiency of the salt could be disrupted by reducing the cation symmetry, thus lowering the melting point. It seems that the asymmetric factor and longer alkyl chains of the cationic porphyrin salt play a key role in achieving the low melting points of these salts.

The nature of the anion affects also significantly the melting point of the porphyrin salts. For these porphyrin-based salts, the influence of tetrakis(perfluorophenyl)-borate groups on the melting point is remarkably obvious and tetrakis(perfluorophenyl)borate porphyrins (**6a**, **6b**, **8**, **10** and **12**) display melting temperatures that are greatly lower than that of bromide or iodide porphyrins (**5a**, **5b**, **7**, **9b** and **11**) (see Table 2). This is probably due to the effective charge distribution over the anion which tends to reduce the crystal lattice energy of the salts, thus resulting in low-melting salts [24].

Conductivity

Table 2 also shows the specific conductivity (κ) of the three liquid porphyrin salts (**5b**, **6b** and **8**) at 22 °C. Indeed, we were not able to measure specific conductivity values for the other salts at higher temperatures. For the salts with the same cation, the specific conductivity is much higher for the $B(C_6F_5)_4^-$ (**6a** and **8**) anion than I^- anion (**5b**). For $B(C_6F_5)_4^-$ anion, the specific conductivity of **6b** (4.01 $mS.cm^{-1}$) is greatly higher than **8** (0.05 $mS.cm^{-1}$). This can be explained by the bigger cation size and molecular weight of the cation of **8** [24].

CONCLUSION

In summary, we have developed an effective synthetic method to prepare porphyrin derivatives bearing one pyridyl or two pyridyl groups by [2+2] aldehyde-dipyrromethane condensation in a one-pot reaction. Alkylation of the neutral porphyrins led to mono- or di-cationic porphyrin salts which were fully characterized by ^1H NMR, ^{19}F NMR, MALDI-TOF mass spectrometry, elemental analysis and UV-visible spectroscopy. DSC studies also indicate that those new ionic liquid porphyrin exhibit relatively low melting points. Furthermore, **5b**, **6b**, and **8** salts are liquid at room temperature and their melting points are observed below 25 °C. These results show that low symmetry of the cation and presence of large anions play an important role in decreasing melting points of these ionic liquid porphyrin derivatives. A specific conductivity value up to 4 $mS.cm^{-1}$ was obtained for a compound (**6b**) having the coordinating anion $B(C_6F_5)_4^-$. Further work on complexation of these ILs is currently underway in our laboratory.

Acknowledgements

The Centre National de Recherche Scientifique (ICMUB, UMR CNRS 5260) is gratefully thanked for financial support. Hai-Jun Xu also gratefully acknowledges the "Région Bourgogne" and CNRS for a post-doctoral fellowship.

Supporting information

^1H and ^{19}F NMR spectra, MALDI-TOF mass spectra and thermal analyses (Figs S1–S46) are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

REFERENCES

1. Welton T. *Coord. Chem. Rev.* 2004; **248**: 2459–2477.
2. Wilkes JS, Levisky JA, Wilson RA and Hussey CL. *Inorg. Chem.* 1982; **21**: 1263–1264.
3. Welton T. *Chem. Rev.* 1999; **99**: 2071–2084.
4. Wasserscheid P and Keim W. *Angew. Chem. Int. Ed.* 2000; **39**: 3773–3789.
5. Seddon KR. *J. Chem. Technol. Biotechnol.* 1997; **68**: 351–356.

6. Ngo HL, Le Compte K, Hargens L and McEwen AB. *Thermochim. Acta.* 2000; **357–358**: 97–102.
7. Hagiwara R. *Electrochemistry* 2002; **70**: 130–136.
8. Gjikaj M, Brockner W, Namysl J and Adam A. *CrystEngComm.* 2008; **10**: 103–110.
9. Dieter KM, Dymek CJ, Heimer NE, Rovang JW and Wilkes JS. *J. Am. Chem. Soc.* 1988; **110**: 2722–2726.
10. Zhan HY, Liu HY, Chen HJ and Jiang HF. *Tetrahedron Lett.* 2009; **50**: 2196–2199.
11. Huddleston JG, Willauer HD, Swatloski RP, Visser AE and Rogers RD. *Chem. Commun.* 1998: 1765–1766.
12. Bosmann A, Datsevich L, Jess A, Lauter A, Schmitz C and Wasserscheid P. *Chem. Commun.* 2001: 2494–2495.
13. Ou ZP, Shen J, Shao JG, Wenbo E, Galezowski M, Gryko DT and Kadish KM. *Inorg. Chem.* 2007: 2775–2786.
14. Endres F and Abedin SZE. *Phys. Chem. Chem. Phys.* 2006; **8**: 2101–2116.
15. Wang P, Zakeeruddin SM, Mozer JE and Grätzel M. *J. Phys. Chem. B* 2003; **107**: 13280–13285.
16. Wang P, Zakeeruddin SM, Comte P, Exnar I and Grätzel M. *J. Am. Chem. Soc.* 2003; **125**: 1166–1167.
17. Matsumoto H, Matsuda T, Tsuda T, Hagiwara R, Ito Y and Miyazaki Y. *Chem. Lett.* 2001: 26–27.
18. Garcia B, Lavallée S, Perron G, Michot C and Armand M. *Electrochim. Acta* 2004; **49**: 4583–4588.
19. Yang SR, Jiang HF, Li YQ, Chen HJ and Xu YB. *Tetrahedron* 2008; **64**: 2930–2937.
20. Dupont J, de Souza RF and Suqrez PAZ. *Chem. Rev.* 2002; **102**: 3667–3692.
21. Carmichael AJ, Earle MJ, Holbery JD, Mc Cormac PB and Seddon KR. *Org. Lett.* 1999; **1**: 997–1000.
22. Zhou ZB, Matsumoto H and Tatsumi K. *Chem. Eur. J* 2006; **12**: 2196–2212.
23. Zhou ZB, Matsumoto H and Tatsumi K. *Chem. Eur. J.* 2005; **11**: 752–766.
24. Zhou ZB, Matsumoto H and Tatsumi K. *Chem. Eur. J.* 2004; **10**: 6581–6591.
25. Reichert WM, Holbrey JD, Swatloski RP, Gutowski KE, Visser AE, Nieuwenhuyzen M, Seddon KR and Rogers RD. *Cryst. Growth Des.* 2007; **7**: 1106–1114.
26. Egashira M, Yamamoto Y, Fukutake T, Yoshimoto N and Morita M. *J. Fluorine Chem.* 2006; **127**: 1261–1264.
27. Langmaier J and Samec Z. *Anal. Chem.* 2009; **81**: 6382–6389.
28. Takai A, Chkounda M, Eggenspiller A, Gros CP, Lachkar M, Barbe JM and Fukuzumi S. *J. Am. Chem. Soc.* 2010; **132**: 4477–4489.
29. Barbe JM, Habermeyer B, Khoury T, Gros CP, Richard P, Chen P and Kadish KM. *Inorg. Chem.* 2010; **49**: 8929–8940.
30. Ohta K, Nguyen-Tran H-D, Tauchi L, Kanai Y, Megumi T and Takagi Y. In *Handbook of Porphyrin Science*, Vol. 12, Kadish KM, Smith KM and Guilard R. (Eds.) World Scientific: New Jersey, 2011; pp 1–120.
31. Huang X, Zhu C, Zhang S, Li W, Guo Y, Zhan X, Liu Y and Bo Z. *Macromolecules* 2008; **41**: 6895–6902.
32. Gust D, Moore TA and Moore AL. *Acc. Chem. Res.* 2009; **42**: 1890–1898.
33. Liu Y, Zhang HJ, Lu Y, Cai YQ and Liu XL. *Green Chem.* 2007; **9**: 1114–1119.
34. Hatay I, Su B, Méndez MA, Corminboeuf C, Khoury T, Gros CP, Bourdillon M, Meyer M, Barbe JM, Ersoz M, Zális S, Samec Z and Girault HH. *J. Am. Chem. Soc.* 2010; **132**: 13733–13741.
35. Boyd PDW and Reed CA. *Acc. Chem. Res.* 2005; **38**: 235–242.
36. Ethirajan M, Chen YH, Joshi P and Pandey RK. *Chem. Soc. Rev.* 2011; **40**: 340–362.
37. Aratani N, Kim D and Osuka A. *Acc. Chem. Res.* 2009; **42**: 1922–1934.
38. Nowak-Krol A, Gryko D and Gryko DT. *Chem. Asian J.* 2010; **5**: 904–909.
39. Maruyama S, Sato K and Iwahashi H. *Chem. Lett.* 2010: 714–716.
40. Romeo C, Sonia IM, Gianbattista P, Canavesi A, Michelucci E, Tiseni PS, Marzorati E, Checchia A, Giannone M, Jabes D, Romanò G, Brunati C, Candiani G and Castiglione F. *J. Med. Chem.* 2007; **50**: 3077–3085.
41. Nakanishi T, Miyashita N, Michinobu T, Wakayama Y, Tsuruoka T, Ariga K and Kurth DG. *J. Am. Chem. Soc.* 2006; **128**: 6328–6329.
42. Ruzié C, Michaudet L and Boitrel B. *Tetrahedron Lett.* 2002; **43**: 7423–7426.