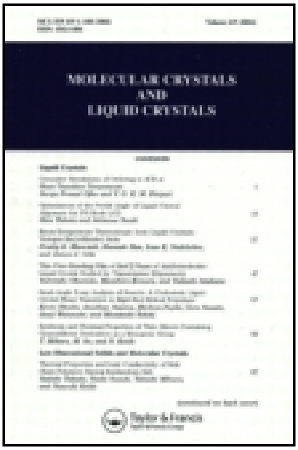

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Columnar Discotic Mesophases from Novel Non-symmetrically Substituted (Octylsulfanyl) Porphyrazines

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Columnar Discotic Mesophases from Novel Non-symmetrically Substituted (Octylsulfanyl) Porphyrazines

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Synthesis and mesomorphism of novel non-symmmetric mono β-aryl (octylsulfanyl)porphyrazines and their Ni(II) complexes were reported. A recently disclosed asymmetrization procedure led to mono β-bromo substituted porphyrazines, which provided access to aryl substituted derivatives through Suzuki cross-coupling. UV-Vis spectroscopy showed a bathochromic shift for bromine and aryl substituted nickel complexes. Optical Microscopy and DSC showed that Br derivatives **3a–3b** *and H-heptakis Ni(II) complex* **2b** *display two columnar mesophases (Col_h and Col_r) stable even at RT and a wide ΔT (100°C). Introduction of the aryl substituent on the macrocycle caused the appearance of only the Col_h mesophase and lower ΔT.*

Keywords: columnar discotic mesophase; non-symmetric porphyrazines; Suzuki cross-coupling

INTRODUCTION

Among the tetrapyrrole macrocycles the porphyrazines display peculiar physical and chemical properties both as ‘free-base’ and as transition metal complexes. Many recent investigations showed their rich coordination chemistry, excellent chemical, thermal and photochemical stability as well as the technological applications of these macrocycles [1,2].

Dedicated to late Professor Augusto Sirigu

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In particular, the alkyl(sulfanyl)porphyrazines, bearing thioether-groups at the β-positions of the azaporphyrin ring, present attractive electrochemical and optical properties as well as high self-organizing capabilities, giving rise to different types of condensed phases such as discotic liquid-crystals (LC) and Langmuir-Blodgett (LB) films. [1*h*-*m*,2] The octakis(alkyl)sulfanylporphyrazine ring can be easily modified by synthetic means, allowing the tuning of the structural and optical properties of the azaporphyrin ring [1*a*-*m*,3]. Such structural flexibility makes these derivatives suitable to investigate in detail the molecular self-organizing phenomena of tetrapyrroles with the aim to find the relationship between the molecular structure and the occurrence of mesophases, with possible applications in opto-electronic technology [1*e*,4]. In recent papers, we have also studied the mesomorphic behaviour of transition metal complexes of octakis alkyl(sulfanyl)porphyrazines [2,5], providing a detailed pattern of the individual role of the size and stiffness of the peripheral tails and of the nature of the metal on the structure and stability of the LC state. Taking into account the great interest risen by non-symmmetric tetrapyrroles and their transition metal complexes, which display a great potential for optical, electrical, catalytic properties and therapeutic application [6], we further studied the self-aggregation properties of non-symmetric alkylsulfanylporphyrazines [7], easily available by a new synthetic route recently disclosed in our laboratories [8]. These studies demonstrated that highly non-symmetric 'free-base' 2,7,8,12,13,17,18-heptakis(octylsulfanyl)-5,10,15,20-porphyrazine **2a** displays discotic mesomorphism, unlike its symmetric counterpart **1a** [2,5]. The same behaviour is shown by 2-bromoheptakis(octylsulfanyl)porphyrazine **3a** derived by simple bromination of **2a**. Probably in these compounds, the permanent dipole induced by the non-symmmetric shape of the macrocycle plays a role in stabilising ordered LC-phases, a feature which might have relevance to the potential application of these discotic molecules in molecular electronics. We then decided to investigate if the peripheral substitution of such non-symmetric porphyrazines with moieties able to modify both their charge distribution and their molecular shape could influence the optical, electrical, and self-aggregation properties of these macrocycles. We then report herein the synthesis of a series of novel non-symmetrically substituted mono β-aryl (octylsulfanyl)porphyrazines and their Ni(II) complexes. A study on the optical and mesomorphic properties of these compounds was then undertaken with the aim to identify the influence of the substituents.

EXPERIMENTAL

General

All chemicals and solvents (Aldrich Chemicals Ltd.) were of reagent grade. Solvents were dried and distilled before use according to standard procedures. Solvents used in physical measurements were of spectroscopic or HPLC grade. Silica gel used for chromatography was Merck Kieselgel 60 (70–230 mesh).

^{1}H and ^{13}C NMR spectra were recorded on an 500 MHz INOVA Varian spectrometer with $SiMe_4$ as internal standard. MALDI-MS spectra were obtained with a MALDI DIE-PRO Applied Biosystems instrument. Samples for mass spectrometric analysis were prepared by depositing 1 μL of porphyrazine solution ($< 10^{-4}$M in CH_2Cl_2) on the probe and allowing this solution to evaporate. 1 μL of the matrix, prepared by dissolving α-cyano-4-hydroxycinnammic acid in CH_3CN-CF_3COOH (70:30, v/v), was then added. MALDI-MS spectra of **4a** and **5b** were obtained with an Ettan MALDI-ToF/Pro (Amersham Biosciences) instrument. The matrix was prepared by dissolving α-cyano-4-hydroxycinnammic acid in CH_3CN-CF_3COOH (100:1, v/v). Samples for mass spectrometric analysis were prepared by dissolving 4 μL of porphyrazine solution ($< 10^{-4}$ M in CH_2Cl_2) directly in 4 μL of the matrix. 0.4 μL of this mixture was deposited on the probe tip and allowed to evaporate. Time-of-flight mass spectrum (TOF) was obtained by irradiating the sample with 10 ns pulses of a Nd(YAG) laser operating at 337 nm. Solution electronic spectra in 1 cm path length quartz cells in the region 250–800 nm were performed on a UV-Vis-NIR 05E Cary spectrophotometer. Optical observations of textures as a function of the temperature were performed with a Axioplan-Zeiss polarizing microscope equipped with a Linkam microfurnace. Images were captured using a Zeiss MC80 Microscope Camera and samples were studied between two silica glass plates (diameter 16.0 mm). Transition temperatures were measured by differential scanning calorimetry with a Perkin-Elmer DSC7 instrument operated at scanning rates of 20°C min^{-1}. The sample pans and covers were made of aluminium (diameter 5.0 mm). The uncertainty in each measured temperature was ±0.1°C.

Syntheses

The symmetrically substituted porphyrazines **1a** and **1b** were prepared according to the procedure previously described in ref [2,5].

The non-symmetrically H-substituted (octylsulfanyl)porphyrazine **2a** and the corresponding Br-substituted porphyrazine **3a** were prepared following the procedure previously reported in ref. [8] and [7], respectively.

[2H-3,7,8,12,13,17,18-Heptakis(octylsulfanyl)-5,10,15,20]-porphyrazinato nickel (II) (2b). The complex was synthesised using the same procedure as for the preparation of the similar heptakis(ethylsulfanyl)-nickel (II) complex [8]. The purification of the resulting dark solid by column chromatography on silica gel using CH_2Cl_2–*n*-hexane (3:7, v/v) as eluent (first band) afforded the desired pure compound (yield *ca.* 30%). ^1H NMR (500 MHz, $CDCl_3$, 297 K), δ/ppm: 8.51 (s, 1 H, pyrrole), 4.11 (t, SCH_2), 4.05 (m, SCH_2), 3.97 (m, SCH_2), 3.79 (t, SCH_2), 3.51 (t, SCH_2), 2.16 (m, CH_2), 1.82 (m, CH_2), 1.55 (m, CH_2), 1.23 (m, CH_2), 0.79 (t, CH_3). UV-Vis ($CHCl_3$) λ_{max}/nm: 328, 338 sh (Soret); 473; 673 (Q band). MALDI-MS: m/z 1381.10 $[M+H]^+$ (calc. 1379.70).

[2-Bromo-3,7,8,12,13,17,18-Heptakis(octylsulfanyl)-5,10,15,20]-porphyrazinato] nickel (II) (3b). The complex was prepared according to ref. [2] and [5] using **3a** as starting porphyrazine. The crude product was passed through a silica gel column using CH_2Cl_2–*n*-hexane (3:7, v/v) as eluent (second band). Removal of the solvent gave a yield of *ca.* 70% of the desired pure compound. ^1H NMR (500 MHz, $CDCl_3$, 297 K), δ/ppm:4.19 (t, SCH_2), 4.01 (m, SCH_2), 3.97 (t, SCH_2), 3.90 (t, SCH_2), 1.85 (m, CH_2), 1.58 (m, CH_2), 1.25 (m, CH_2), 0.80 (t, CH_3). UV-Vis ($CHCl_3$), λ_{max}/nm: 328, 340 sh (Soret); 485; 661 (Q band). MALDI-MS: m/z 1460.03 $[M+H]^+$ (calc. 1457.62).

Suzuki Cross-Coupling Reaction. General Procedure

Non-symmetric brominated porphyrazine **3a** or **3b** (0.07 mmol), potassium carbonate (0.56 mmol), tetrakis(triphenylphosphine)-palladium (0) (10%mol) and the corresponding boronic acid (0.28 mmol) were refluxed in a dry DMF/toluene (2:3, v/v) mixture (10 mL) under N_2. The reaction was stopped after 18 h or after 4 h when the substrate was **3a** or **3b**, respectively. After cooling to room temperature water was added and the solution was extracted with CH_2Cl_2. The organic fractions were collected, dried over sodium sulphate and filtered. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using a CH_2Cl_2–*n*-hexane mixture as eluent.

2-Phenyl-3,7,8,12,13,17,18-Heptakis(octylsulfanyl)-5,10,15,20-21H, 23H-porphyrazine (4a). According to the conditions of the General

Procedure the reaction of 'free-base' **3a** with phenylboronic acid resulted in the isolation of **4a** after purification by chromatography on silica gel with a CH_2Cl_2-n-hexane (4:6) mixture as eluent (third band). Yield *ca.* 20%. ^{1}H NMR (500 MHz, $CDCl_3$, 297 K), δ/ppm: 8.38 (d, 2H), 7.76 (t, 2H), 7.64 (t, 1H), 4.12 (m, SCH_2), 4.02 (m, SCH_2), 3.90 (t, SCH_2), 1.85 (m, CH_2), 1.55 (m, CH_2), 1.20 (m, CH_2), 0.88 (m, CH_3), 0.78 (m, CH_3), -1.12 (s, NH). UV-Vis ($CHCl_3$), λ_{max}/nm: 363, (Soret); 503; 639, 708 (Q bands). MALDI-MS: m/z 1400.12 $[M+H]^+$ (calc. 1399.82).

[2-Phenyl-3,7,8,12,13,17,18-Heptakis(octylsulfanyl)-5,10,15,20]-porphyrazinato] nickel (II) (4b). The reaction of nickel(II) complex **3b** and phenylboronic acid gave the desired pure β-arylated porphyrazine **4b** after chromatographic purification on silica gel with a CH_2Cl_2-n-hexane (4:6) mixture as eluent (second band). Yield *ca.* 30%. ^{1}H NMR (500 MHz, $CDCl_3$, 297 K), δ/ppm: 8.32 (d, 2H), 7.73(t, 2H), 7.62 (t, 1H), 4.03 (m, SCH_2), 3.96 (t, SCH_2), 3.77 (t, SCH_2), 1.85 (m, CH_2), 1.55 (m, CH_2), 1.20 (m, CH_2), 0.78 (m, CH_3). UV-Vis ($CHCl_3$), λ_{max}/nm: 332, 341 sh (Soret); 488; 665 (Q band). MALDI-MS: m/z 1457.21 $[M+H]^+$ (calc. 1455.74).

2-(4-biphenyl)-3,7,8,12,13,17,18-Heptakis(octylsulfanyl)-5,10,15,20–21H,23H-porphyrazine (5a). Reaction of 'free-base' **3a** with biphenylboronic acid resulted in the isolation of **5a** after purification by chromatography on silica gel with a CH_2Cl_2-n-hexane (4:6) mixture as eluent (third band). Yield *ca.* 20%. ^{1}H NMR (500 MHz, $CDCl_3$, 297 K), δ/ppm: 8.53 (d, 2H), 8.02 (d, 2H), 7.84 (d, 2H), 7.56 (t, 1H), 7.45 (d, 2H), 4.12 (m, SCH_2), 4.02 (t, SCH_2), 3.98 (t, SCH_2), 3.94 (t, SCH_2), 1.89 (m, CH_2), 1.55 (m, CH_2), 1.19 (m, CH_2), 0.88 (m, CH_3), 0.79 (m, CH_3), -1.09 (s, NH). UV-Vis ($CHCl_3$), λ_{max}/nm: 346, 3.62 sh) (Soret); 507; 639, 710 (Q bands). MALDI-MS: m/z 1477.10 $[M+H]^+$ (calc. 1475.85).

[2-(4-biphenyl)-3,7,8,12,13,17,18-Heptakis(octylsulfanyl)-5,10,15,20]–porphyrazinato] nickel (II) (5b). From the reaction of **3b** with biphenylboronic acid was isolated **5b** after purification by chromatography on silica gel with a CH_2Cl_2–n-hexane (4:6) mixture as eluent (second band). Yield *ca.* 50%. ^{1}H NMR (500 MHz, $CDCl_3$, 297 K), δ/ppm: 8.47 (d, 2H), 8.00 (d, 2H), 7.84 (d, 2H), 7.56 (t, 1H), 7.46 (d, 2H), 4.05 (m, SCH_2), 3.98 (t, SCH_2), 3.86 (t, SCH_2), 3.81 (t, SCH_2), 1.85 (m, CH_2), 1.55 (m, CH_2), 1.21 (m, CH_2), 0.80 (m, CH_3). UV-Vis ($CHCl_3$), λ_{max}/nm: 327, 338 sh (Soret); 487, 664 (Q band). MALDI-MS: m/z 1532.70 $[M+H]^+$ (calc. 1531.77).

[2-(4-N,N-dimethylammino-Phenyl)-3,7,8,12,13,17,18-Heptakis-(octylsulfanyl)-5,10,15,20]–porphyrazinato] nickel (II) (6). Following the general procedure the reaction of nickel(II) complex 3b and

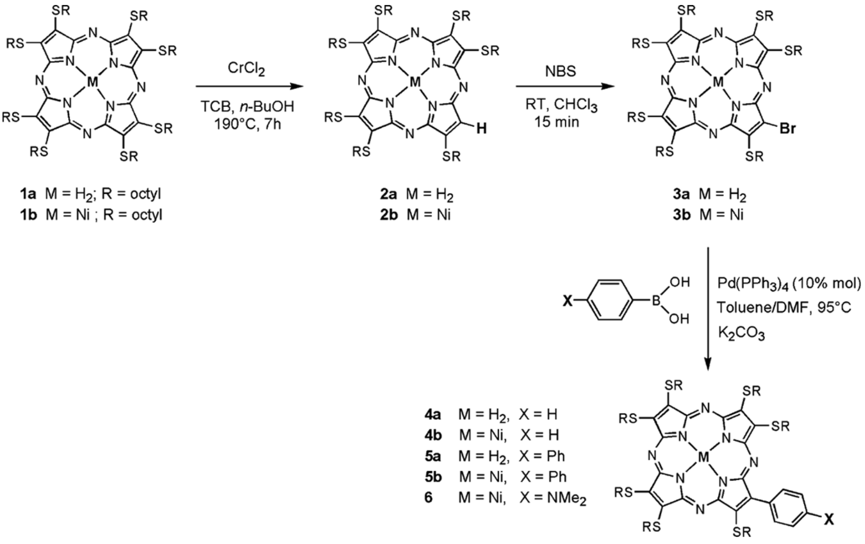
4-N,N-dimethylammino-phenylboronic acid led to the isolation of **6** after chromatographic purification on silica gel with a CH_2Cl_2–*n*-hexane (4:6) mixture as eluent (second band). Yield *ca.* 30%. ^{1}H NMR (500 MHz, $CDCl_3$, 297 K), δ/ppm: 8.44 (d, 2H), 7.08 (d, 2H), 4.02 (m, SCH_2), 3.83 (t, SCH_2), 3.79(t, SCH_2), 3.18 (s, CH_3), 1.84 (m, CH_2), 1.56 (m, CH_2), 1.20 (m, CH_2), 0.78 (t, CH_3). UV-Vis ($CHCl_3$), λ_{max}/nm: nm: 328, 340 sh (Soret); 513; 669, 694 sh (Q bands), 750. MALDI-MS: m/z 1499.51 $[M+H]^+$ (calc. 1498.78).

RESULTS AND DISCUSSION

Synthesis

We recently set up [8] a new preparative strategy (Scheme 1) to highly non-symmetric (alkylsulfanyl)porphyrazines by hydrogen replacement of one alkylsulfanyl tail of the fully substituted porphyrazines **1**, resulting in the non-symmetrical β-H-substituted porphyrazines **2**.

Such approach displays the great advantage of a very clean reaction, easy purification procedures and yield larger then 40% of the desired non-symmetrically substituted product. The subsequent one-step replacement of the pyrrole β-hydrogen of **2** by a bromine atom leads to **3**, suitable intermediates for introducing different substituents on the macrocycle [7]. Herein we show that the easily accessible



SCHEME 1 Synthesis if non-symmetrically substituted (octylsulfanyl) porphyrazines.

mono-bromo porphyrazines **3** can be then efficiently arylated by Pd-catalysed Suzuki coupling reactions [9], providing access to a wide range of non-symmetric β-aryl substituted derivatives **4–6**.

According to our protocol, symmetric 'free-base' and Ni(II) metalated porphyrazines **1a** and **1b** were treated with the one-electron donor $CrCl_2$, leading to the non-symmetric **2a,b** [8]. The latter were then brominated with NBS, affording **3a,b** [7]. The brominated compounds were then submitted to Suzuki cross-coupling, by reaction with the corresponding boronic acid in the presence of excess of K_2CO_3 and catalytical amounts of $Pd(PPh_3)_4$ (10%mol). Spectral data (^{1}H NMR, MALDI-MS) of arylated products were consistent with assigned formulations.

To the best of our knowledge these are the first examples of Suzuki cross coupling reactions on porphyrazine macrocycles. Following this approach we introduced aryl moieties that we expected to exert specific shape and electronic effects on the macrocycles influencing their aggregation properties. The phenyl (**4**) and biphenyl (**5**) groups were chosen for their mainly steric effects, while the 4-*N*,*N*-dimethylamminophenyl moiety in **6** was expected also to act as an electron donor, giving rise to a push-pull system, suitable for molecular electronics. Preliminary DFT computations shows, [10,11] in fact, that in all the studied aryl substituted porphyrazines the LUMO, LUMO + 1, and the HOMO are porphyrazine-localised orbitals, whereas only in the case 4-NMe_2Ph substituted complex **6**, the HOMO is localized on the phenyl ring and characterized by less negative energy value (Fig. 1).

Furthermore according to TDDFT computations the first excited state of **6** can be assigned to the HOMO-LUMO transition, with a strong charge transfer from the phenyl ring to the porphyrazine ring. The existence of this excited state is confirmed by the higher absorbance at longer wavelengths in the UV-Vis spectra (*vide infra*).

Interestingly, the Suzuki coupling on the 'free base' brominated heptakis-octylthio porphyrazine **3a** was very sluggish, while the same reaction provided higher yields and faster reaction when performed on the Ni(II) complex **3b**. This behaviour resembles what observed in the case of metal-catalyzed cross coupling on porphyrin macrocycles [12].

Spectroscopy

The substituent effect on the optical properties of the studied non-symmetric porphyrazines were investigated by UV-Vis absorption spectroscopy of their Ni(II) complexes. The optical spectra ($CHCl_3$) of the non-symmetric Ni(II) porphyrazine **2b** shows an intense band at ≈328 nm (Soret band), an almost equally intense band at ≈673 nm (Q band) and an absorption at about 473 nm ("extra band") (Fig. 2) [13].

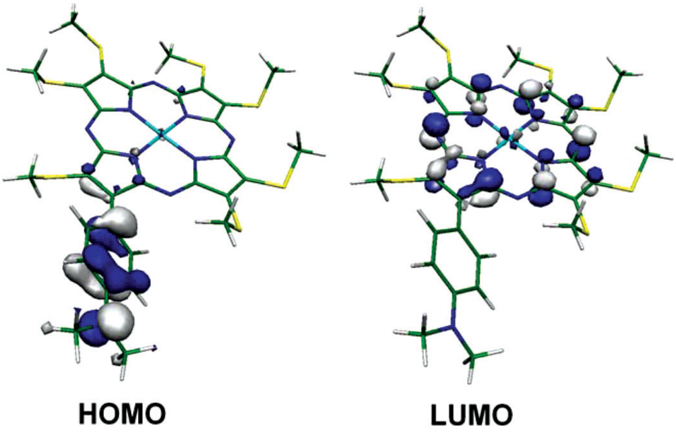


FIGURE 1 Computed HOMO and LUMO Kohn-Sham orbitals of **6**.

The main spectral change in respect to the symmetric parent **1b** is the observed blue shift (10–15 nm) of the extra band, as already observed in non-symmetric S-ethyl substituted porphyrazines [8]. The macrocycle substitution with bromine, phenyl and biphenyl moieties induces, on the contrary, a red shift (12–15 nm) in the

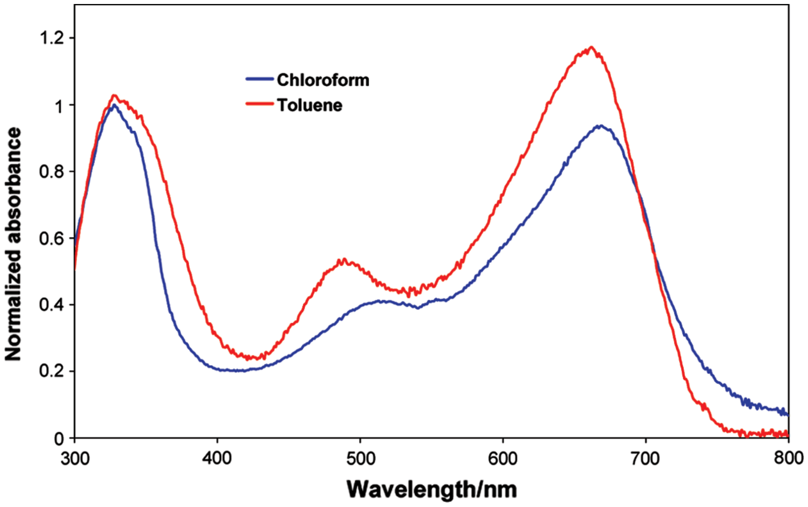


FIGURE 2 UV-Vis spectra in $CHCl_3$; scan rate 600 nm/min.

400–550 nm range in respect to **2b**. As inferred from Figure 2, the shift is further increased up to 40 nm in 4-NMe_2-phenyl substituted complex **6**, which also display a widening of the Q band (≈669 nm). Such bathochromic shifts reflect an effective electronic delocalization between the porphyrazine core and the peripheral aryl groups, as observed in the case of tetrakis arylethynyl substituted porphyrins [14], and make these compounds very attractive for application in non-linear optics [15]. The peculiar spectral behaviour of the 4-*N*,*N*-dimethylaminophenyl substituted compound **6** is also confirmed by its evident solvatochromism, not displayed by the other studied complexes.

As inferred from the optical spectra of **6** (Fig. 3) the Q and the extra bands exhibit strong ipsochromism when passing from $CHCl_3$ to toluene, shifting to the blue by 24 nm and 7 nm, respectively. In toluene are also removed other typical spectral features of this compound like the marked asymmetry of the extra band and the weak absorption at longer wavelengths (780 nm).

Mesomorphism

To gain insight on the effect of peripheral substitution on the self-organizing capability of the non-symmetric porphyrazines in LC phases, we studied the mesomorphic behavior of the synthesized

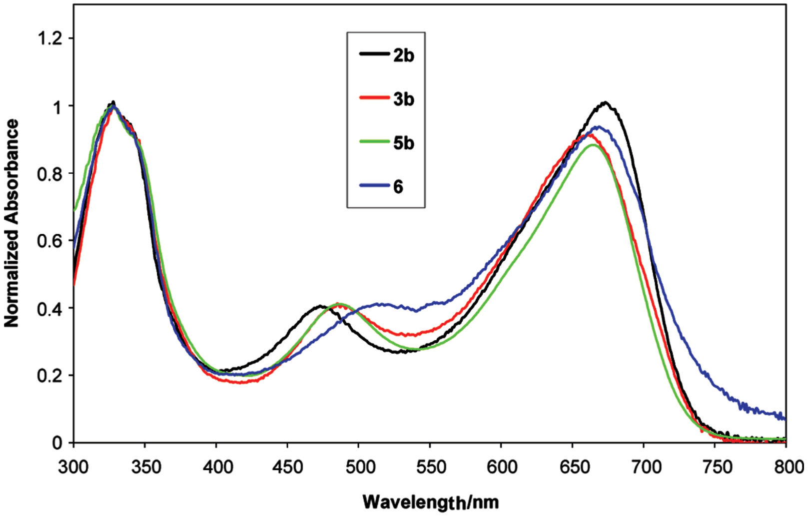


FIGURE 3 UV-Vis spectra of compound **6** in $CHCl_3$ and toluene; scan rate 600 nm/min.

'free-base' and nickel compounds using DSC and polarizing microscopy. In Table 1 the thermal phase transitions data collected for all the studied compounds are reported and compared with literature data for compounds **1a-b** [2], **2a**, and **3a** [7].

The optical microscopic observations were performed placing the sample between two glass slides. Values of the mesophase thermal stability range (ΔT) were usually measured cooling the isotropic melt. In fact, on cooling the mesophase textures and phase transitions were best resolved. In some compounds the presence of two different mesophases and the temperatures of their transitions could be detected only by optical analysis. In many cases the samples obtained from evaporation of solutions exhibited at room temperature viscous and birefringent trace when rubbed on the glass plate and observed

TABLE 1 Optical and Thermal Properties of Compounds **1–6**

Compound	Phase transitions T(°C)[a]	Thermal stability range ΔT(°C)
1a	K 81.5 I[b]	–
1b	K 67.6 Col$_h$ 118.8 I[b]	51.2
2a	K 51.7 Col$_h$ 99.7 I[c]	48.2
	I 92 Col$_h$-5 K	97.0
2b	M 51.7 Col$_h$ 92.5 I	Col$_h$ 40.8
	I 71.8 Col$_h$ 8.0 Col$_r$–30.0 K	Col$_h$ 63.8; Col$_r$ 38 ΔT_{tot} 101.8
3a	K 37.3 Col$_h$ 113.7 I[c]	76.4
	I 105.2 Col$_h$ 28.0 Col$_r$ 3.5 K	Col$_h$ 77.2; Col$_r$ 24.5 ΔT_{tot} 101.7
3b	M 47.4 Col$_h$ 120.0 I	Col$_h$ 72.6
	I 92.0 Col$_h$ 35.1 Col$_r$ 7.0 K	Col$_h$ 56.9; Col$_r$ 28.1 ΔT_{tot} 85.0
4a	K 46.2 I	–
	I 38.5 K	–
4b	M 43.4 I	–
	I 37.0 Col 1.0 K	36.0
5a	M 77.2 I	–
	I 57.0 Col$_h$ 43.0 K	14.0
5b	M 62.5 I	
	I 39.5 Col$_h$ 27.0 K	12.5
6	K 77.1 I	–
	I 27.7 K	–

[a] First line report transition temperatures measured on heating, second line report temperatures on cooling. K = solid, M = unidentified mesophase, Col$_r$ = columnar rectangular mesophase, Col$_h$ = columnar hexagonal mesophase, I = isotropic liquid.

[b] Data taken from ref. [2].

[c] Data taken from ref. [7].

under crossed polarizers. This behavior was typical of a LC phase [16,17] therefore, even if the texture of the mesophase was not detectable, we defined these phases as "unidentified mesophase" (M) in Table 1. The calorimetric analysis (Table 1) points out that all the investigated compounds display enantiotropic mesomorphism, being the reverse phase transformations always well resolved, although some supercooling of the transitions did regularly occur.

In the 'free base' porphyrazines the substitution of one of the peripheral S-alkyl chain with a H atom in **2a**, induces the appearance of an ordered mesophase, not present in the parent symmetric azamacrocycle **1a**. This compound displays focal-conic or fan-shaped texture, typical of columnar hexagonal mesophases (Col_h) [2,5,16–18]. The introduction of Ni inside the macrocycle ring enhances, both in symmetric and non-symmetric porphyrazines, the mesomorphic behaviour. In fact, earlier studies [2] showed that even though symmetric 'free base' counterpart **1a** misses the LC phase, its Ni complex **1b** displays a Col_h mesophase. The non-symmetric Ni complex **2b** displays very interesting liquid crystalline properties. During the first heating of the viscous phase of **2b**, obtained by solution evaporation, the typical focal-conic texture of the Col_h mesophase appeared at 51.7°C and cleared at 95.2°C. Subsequent fast (20°C/min) cooling from the isotropic liquid led at 71.8°C (after a supercooling of *ca.* 23°C) to the appearance, under crossed-polarizer, of focal-conic texture and of hexagonal dendritic structures, more clearly visible without crossed polarizers, both related to a Col_h mesophase [18,19,20]. This LC phase evolved, at 8.0°C, to a fingerprint texture which is usually displayed by columnar rectangular mesophases (Col_r) [18,20,21]. Finally, further cooling led to crystallization of the sample at -30°C. The measured liquid crystalline ΔT for **2b** (101.8°C) was then wider both of the one of its non-symmetric 'free base' **2a** and of the symmetric Ni complex **1b**. A similar behavior was displayed by the bromine substituted non-symmetric porphyrazine **3a** and by its Ni complex **3b** (Fig. 4).

In both compounds, upon cooling from the isotropic liquid a transition from a Col_h to a Col_r LC phase was observed. The stability ranges of their mesophases were comparable with the ones displayed by the H substituted porphyrazines **2a** and **2b** but, surprisingly, the Br substituted Ni complex **3b** showed lower ΔT than the 'free base' counterpart **3a**. It is noteworthy that all the non-symmetric porphyrazines **2a–3a** and their Ni(II) complexes **2b–3b** display a wide range of mesophase stability and that their columnar arrangement is retained until well below room temperature. Such tendency of the molecules to maintain the same organization at low temperatures is important for the preparation of single-domain LC films required for

FIGURE 4 Liquid-crystalline textures shown on cooling by **3b** at 77°C (*top*) and at 18°C (*bottom*). Crossed polarizers microscope.

photovoltaic applications [17,19]. Against all cursory expectation, in these compounds the less ordered mesophase Col_r was observed at lower temperature than the most ordered Col_h phase, a behaviour recently observed in columnar LC of non-symmmetrically substituted porphyrins [16].

As inferred from Table 1 the β-aryl substitution of the porphyrazines in **4–6** destabilizes the mesomorphic properties of these azamacrocycles. Also in these cases, however, the introduction of the Ni within the macrocycle provides higher stabilization of the mesophases.

The phenyl-substituted 'free base' porphyrazine **4a** does not show any mesomorphic behaviour, while its Ni(II) complex **4b** exhibits a liquid-crystalline texture (between 1°C and 37°C) as shown in Figure 5 (top).

The presence of a biphenyl substituent induces the formation of a stable Col_h mesophase even in the 'free base' porphyrazine **5a** (Fig. 5, bottom), although displaying a quite small thermal stability range (14°C). A small ΔT is also observed in the corresponding Ni(II) complex **5b**, which shows a columnar hexagonal LC phase between

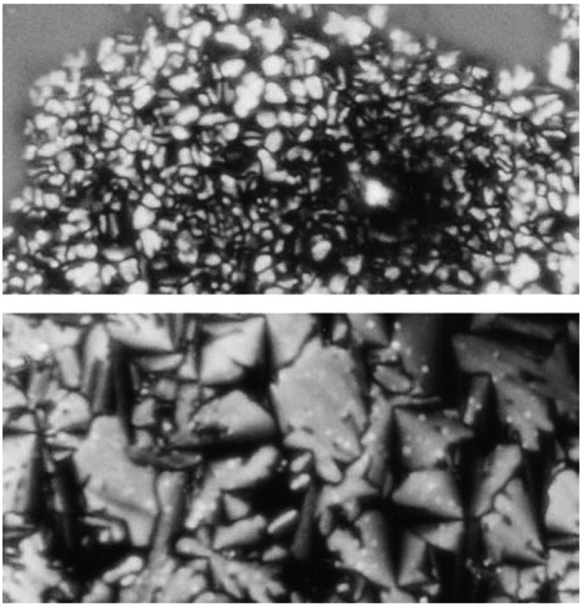


FIGURE 5 (*top*) Liquid-crystalline texture shown on cooling by **4b** at 20°C; (*bottom*) Liquid-crystalline textures shown on cooling by **5a** at 49°C. Crossed polarizers microscope.

27.0°C and 39.5°C. As already observed for compounds **2a,b–3a,b** the aryl substituted Ni complex **4b** displays mesomorphic behaviour at room temperature, even if with a rather low T_i (37°C). It is then possible that the aryl moieties sterically interfere with the intermolecular interactions responsible of the mesomorphic aggregation. Unfortunately, also the 4-*N*,*N*-dimethylamminophenyl substituted derivative **6**, which, on the basis of calculations and spectral analysis (*vide supra*), was the most promising one for applications in NLO, did not show any mesophase. This behaviour could be due to the competition between S and N interactions with Ni in the porphyrazine core. Work is in progress for clarifying the origin of this behaviour in order to design new derivatives displaying at the same time charge-tranfer properties and more stable ordered mesophases.

In alkyl(thio)porphyrazines the formation of LC phases is determined by the concomitant presence of different intermolecular forces, as π–π interactions between the aromatic rings (for the 'free-base' azaporphyrins), Van der Waals interactions of the peripheral chains, static dipole-dipole interactions (for the non-symmetric porphyrazines), and metal-sulfur interactions between adjacent rings (for metalloporphyrazines) [1*h*-*m*,2,3,5,7,22]. Furthermore, from a ΔG point of view the different availability of side chains torsional states might have large influence on the ΔS contribution on the phase transition temperatures [23].

Molecular Dynamics simulations [23] have shown that on cooling a starting organization of the porphyrazine core is necessary. This means that core-core interactions are the driving force for the achievements of columnar organization. In this respect the most interesting parameter is represented by the isotropization temperature (T_i). Considering the temperature values reported in Table 1 it is possible to suggest that the two most relevant interactions are the static dipole-dipole and the metal-heteroatom ones [3*c*–*d*,5,7] complemented by strong stereochemical perturbation due either to the very large moieties like the biphenyl or to the very small H- substituent. In fact, the T_i value decreases as follow **3b** > **1b** > **3a** > **2a** > **2b** >> **5a** > **5b**. The largest value of T_i for **3b** is probably due both to the larger dipole than **1b** and to the fact that the Br atom achieves the same interation toward Ni as S atom does. On the other hand, **3a** has a larger dipole than **2a** and thus more significant dipole-dipole interactions occur. In the case of **2b** the “hole” in the peripheral substitution of the macrocycle probably determines a large perturbation in the ordering of the side chains during the liquid to mesophase transition and increases the entropy due to a large number of S-Ni interactions. The more stiff and bulky biphenyl substituent engenders very large perturbation in the stacking and thus decreases the conformational freedom of the side chains.

CONCLUSIONS

We described herein the synthesis of novel non-symmmetric β-aryl (octylsulfanyl) porphyrazines by applying, for the first time on these macrocycles, the palladium-catalyzed Suzuki cross-coupling reactions. The electronic effects of the aryl substitution were investigated by UV-Vis absorption spectroscopy of their Ni(II) complexes, observing in all these compounds a spectral red shift in the 400–550 nm range, more pronounced in the case of 4-NMe_2-phenyl substituted complex **6**, which also displays a Q band widening. Such bathochromic shifts reflect an actual electronic interplay between the porphyrazine core and the peripheral aryl groups making these compounds very attractive for application in non-linear optics. These non-symmetric porphyrazines as well as their H- and Br-substituted parent compounds, showed also very interesting mesomorphic properties. Compounds **3a** and **3b** showed the most remarkable liquid-crystal behaviour, displaying two columnar mesophase, hexagonal and rectangular, the latter being stable until well below room temperature. In these compounds a very wide thermal stability range was observed (*ca.* 100°C), making them very attractive for technological applications. On the other hand, the aryl substituted non-symmetric derivatives, although displaying promising charge-transfer properties, showed hexagonal columnar mesophases with lower ΔT and melting temperature values. Although the aryl substituted porphyrazines **4–6** are then not suitable for LC application yet, this study shows that it is possible to obtain porphyrazine macrocycle displaying both mesomorphic and charge-transfer properties. The synthetic approach followed herein then discloses the way to a wide range of molecular architectures, allowing the tuning of the electronic and mesomorphic properties of these macrocycles by insertion of suitable moieties capable of extending the electronic conjugation and stabilizing the intermolecular interactions. Further work is in progress in our laboratory in order to match useful technological properties for this class of molecules.

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