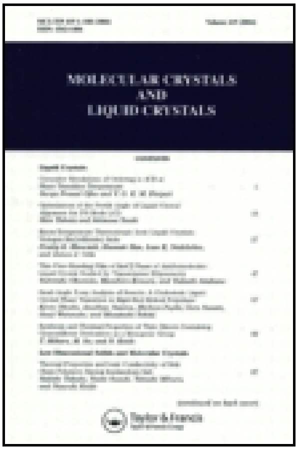

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Discotic Liquid Crystals of Transition Metal Complexes 9: Synthesis and Properties of Discotic Liquid Crystals of Tetrapyrazinoporphyrazine Derivatives

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Discotic Liquid Crystals of Transition Metal Complexes 9: Synthesis and Properties of Discotic Liquid Crystals of Tetrapyrazinoporphyrazine Derivatives

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Octa(dodecyl)tetrapyrazinoporphyrazine $(C_{12})_8P_zH_2$, the corresponding metal (II) complexes $(C_{12})_8P_zM$, M: Cu, Ni, Co, octa(2-ethylhexyl)tetrapyrazinoporphyrazine $(2\text{-}EtC_6)_8P_zH_2$ and the corresponding copper (II) complex $(2\text{-}EtC_6)_8PzCu$ have been synthesized and their liquid crystalline states characterized. These properties have been compared to those of the corresponding phthalocyanines. The metal free $(C_{12})_8P_zH_2$ derivative forms a hexagonal disordered columnar mesophase (D_{hd}) like $(C_{12})_8PcH_2$, whereas $(C_{12})_8P_zM$ (M: Cu, Ni, Co) lead to centered rectangular disordered columnar mesophases (D_{rd}). The branched chain substituted metal free derivative $(2\text{-}EtC_6)_8P_zH_2$ leads to a tetragonal mesophase as $(2\text{-}EtC_6O)_8PcH_2$. $(2\text{-}EtC_6O)_8PcCu$ forms an oblique mesophase, whereas $(2\text{-}EtC_6)_8P_zCu$ leads to an unidentified liquid crystal. The tetrapyrazinoporphyrazine compounds are the first π-acceptor columnar mesogens; the half-wave reduction potentials are −0.41 V for $(C_{12})_8P_zH_2$ and −0.55 V for $(C_{12})_8P_zM$ (M: Cu, Ni). In comparison, phthalocyanine derivatives are reduced at −0.94 V for $(2\text{-}EtC_6O)_8PcH_2$ and −1.05 V for $(2\text{-}EtC_6O)_8PcZn$.

Keywords: Tetrapyrazinoporphyrazine complexes, liquid crystals, molecular materials, phthalocyanine complexes

INTRODUCTION

Tetrapyrazinoporphyrazine[2] is a phthalocyanine analogue with nitrogen atom replacing carbon at position 1,4,10,13,22,28,31 (Figure 1). Pyrazine moieties are good electron acceptors.[2] Substituted phthalocyanines are, on the other hand, well known to form columnar (discotic) liquid crystals.[3,4] This paper describes the synthesis and the liquid crystalline properties of π-acceptor columnar mesogens based on the tetrapyrazinoporphyrazine subunit. Discotic mesophases can form submicronic

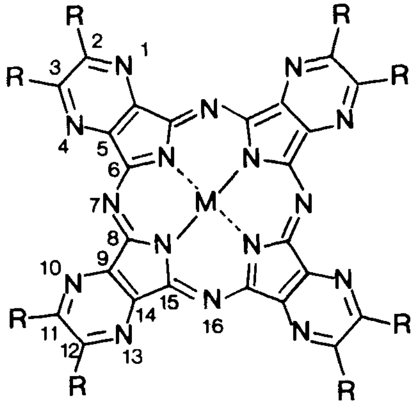


FIGURE 1 The various substituted tetrapyrazinoporphyrazine derivatives which have been synthesized.
3: $(C_{12})_8PzM$ R = $C_{12}H_{25}$ M = 2H (a); Cu (b); Ni (c); Co (d)
4: $(2\text{-EtC}_6)_8PzM$ R = 2-Ethylhexyl M = 2H (a); Cu (b)

one-dimensional conductors when the concentration of charge carriers is sufficiently high.[3,16] The use of electron donor and electron acceptor discogens permits to envisage the generation of carriers via a charge transfer process.

A preliminary report has been published[5] describing, at that time, the first π-acceptor discogens.

$(2\text{-EtC}_6)_8PzH_2$ and $(2\text{-EtC}_6)_8PzCu$ have been synthesized to investigate the effect of branched alkyl chain on the structure of the mesophases. Previous studies showed that branched chains can lead to lenticular nematic liquid crystals.[6] $(C_{12})_8PzM$ (M: Cu, Ni, Co) present centered rectangular disordered columnar (D_{rd}) mesophases. $(2\text{-EtC}_6)_8PzH_2$ forms a tetragonal mesophase which structure is very similar to the corresponding phthalocyanine $(2\text{-EtC}_6O)_8PcH_2$.

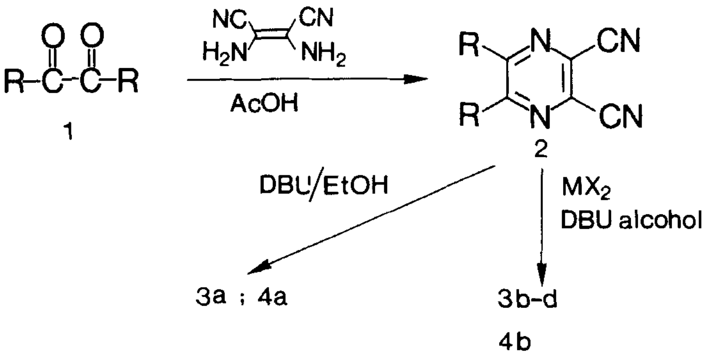
EXPERIMENTAL

Synthesis

The synthetic route for synthesizing the tetrapyrazinoporphyrazine derivatives $(C_{12})_8PzM$ (M = 2H: 3a, M = Cu: 3b, M = Ni: 3c, M = Co: 3d) and $(2\text{-EtC}_6)_8PzM$ (M = 2H: 4a, M = Cu: 4b), is given in Scheme 1. The starting material, (1), was prepared by the method described in previous papers.[7] The dicyanopyrazine derivatives (2) were synthesized by the method of K. Kanakarajan et al.[8] The tetrapyrazinoporphyrazine derivatives (3a, 4a) were obtained by the method of H. Tomoda et al.[9] Elemental analyses of the final products and the conditions used to transform 2 into 3 (reaction media, recrystallization solvents, yield) are listed in Table I.

2,3-Dicyano-4,5-didodecylpyrazine (2, R = $C_{12}H_{25}$)

A mixture of 2.5 g (6.1 mmol) of hexacosane-13,14-dione (1, R = $C_{12}H_{25}$) and 1.6 g (15 mmol) of diaminomaleonitrile in 120 ml of acetic acid was refluxed for



SCHEME I The chemical pathway used to synthesize the substituted tetrapyrazinoporphyrazine derivatives.

TABLE I

Elemental analyses of 3a–d and 4a, b, reaction media, recrystallization solvents and yields for the reaction starting from the dicyano-derivative 2

Compound	Molecular Formula	Elemental Analysis Calcd. % (Found%) N	C	H	Reaction solvent	Recryst. solvent	Yield (%)
3a $(C_{12})_8PzH_2$	$C_{120}H_{202}N_{16}$ (1869.05)	11.99 (11.97)	77.12 (77.06)	10.89 (10.84)	EtOH	THF	14
3b $(C_{12})_8PzCu$	$C_{120}H_{200}N_{16}Cu$ (1930.58)	11.61 (11.38)	74.66 (74.75)	10.44 (10.45)	PrOH	AcOEt + CH_2Cl_2	8
3c $(C_{12})_8PzNi$	$C_{120}H_{200}N_{16}Ni$ (1925.72)	11.64 (11.74)	74.85 (74.62)	10.47 (10.47)	$CH_3OC_2H_4OH$	THF	16
3d $(C_{12})_8PzCo$	$C_{120}H_{200}N_{16}Co$ (1925.97)	11.64 (11.98)	74.84 (74.57)	10.47 (10.80)	$C_5H_{11}OH$	n-hexane	20
4a $(Et\text{-}C_6)_8PzH_2$	$C_{88}H_{138}N_{16}$ (1420.18)	15.78 (15.68)	74.42 (72.90)	9.80 (9.52)	EtOH	CH_3CN	22
4b $(2Et\text{-}C_6)_8PzCu$	$C_{88}H_{136}N_{16}Cu$ (1481.71)	15.13 (14.38)	71.33 (68.58)	9.25 (9.21)	PrOH	AcOEt + EtOH	18

12 h. After cooling to room temperature, the mixture was extracted with diethylether and washed with water. The organic solution was dried over sodium sulfate and evaporated to dryness to give a brown solid. The crude product was purified by column chromatography (silica gel, chloroform, R_f = 0.80). White crystals, Yield: 2.4 g (85%), m.p. = 44°C.

^{1}H-NMR ($CDCl_3$: TMS) δ 2.7 (t, 4H) 1.3 (m, 40H) 0.9 (t, 6H).

IR (KBr, cm^{-1}) ν 2940, 2860 (CH_2), 2250 (CN).

MS (m/e): 467 (M^+ + 1).

2,3-Dicyano-4,5-(2-ethylhexyl)pyrazine (2, R = 2-ethylhexyl)

The compound was prepared by the same procedure as for the 2,3-dicyano-4,5-didodecylpyrazine (2, R = $C_{12}H_{25}$). The purification was carried out by column chromatography (silica gel, dichloromethane, n-hexane, 2:1 (v/v), R_f = 0.64). Yellow oily liquid, Yield: 36%.

^{1}H-NMR ($CDCl_3$: TMS) δ 2.83 (d, 4H) 1.23 (m, 18H) 0.90 (m, 12H).

IR (neat, cm^{-1}) ν 2990, 2950 (CH_2), 2250 (CN).

MS (m/e): 355 (M^+ + 1).

5,6,5′,6′,5″,6″,5‴,6‴-Octa(dodecyl)tetrapyrazino [2,3-b: 2′,3′-g: 2″,3″-l: 2‴,3‴-q]-porphyrazine $(C_{12})_8PzH_2$: 3a

A mixture of 2.0 g (4.3 mmol) of the dicyanopyrazine derivative (2, R = $C_{12}H_{25}$) and 0.98 g (6.5 mmol) of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) in 15 ml of ethanol under nitrogen was refluxed for 20 h. At room temperature, the mixture was extracted with chloroform and washed with water. The organic solution was dried over sodium sulfate and evaporated to dryness to give the crude product. The purification was carried out by column chromatography (silica gel, dichloromethane, R_f = 0.86) and recrystallization from tetrahydrofuran (THF). Yield: 14%.

^{1}H-NMR (250 MHz, $CDCl_3$: TMS) δ 3.55 (t, 16H, CH_2) 2.88 (quint., 16H, CH_2) 1.73 (quint., 16H, CH_2) 1.54 (quint., 16H, CH_2) 1.28 (m, 112H, CH_2) 0.88 (t, 24H, CH_3) −1.46 (s, 2H, NH).

5,6,5′,6′,5″,6″,5‴,6‴-Octa(2-ethylhexyl)tetrapyrazino [2,3-b: 2′,3′-g: 2″,3″-l: 2‴,3‴-q]-porphyrazine $(2\text{-}EtC_6)_8PzH_2$: 4a

The compound was prepared by the same procedure as for 3a. The purification was carried out by column chromatography (silica gel, dichloromethane, R_f = 0.80) and recrystallization from acetonitrile.

^{1}H-NMR (250 MHz, $CDCl_3$: TMS) δ 3.52 (d, 16H, CH_2) 2.57 (quint., 8H, CH) 1.66 ~ 1.33 (m, 64H, CH_2) 1.08 (t, 24H, CH_3) 0.91 (t, 24H, CH_3) −0.04 (s, 2H, NH).

5,6,5′,6′,5″,6″,5‴,6‴-Octa(dodecyl)tetrapyrazino [2,3-b: 2′,3′-g: 2″,3″-l: 2‴,3‴-q]-porphyrazinato copper (II) complex $(C_{12})_8PzCu$: 3b

A mixture of 5.0 g (11 mmol) of the dicyanopyrazine derivative (2, R = $C_{12}H_{25}$), 0.36 g (2.8 mmol) of copper (II) chloride, and 2.5 g (17 mmol) of DBU in 35 ml of n-propanol was refluxed for 20 h. The mixture was extracted at room temperature with chloroform and washed with water. The solution was dried over sodium sulfate and the solvent was evaporated to dryness. The purification of the product was carried out by column chromatography (silica gel, dichloromethane, R_f = 0.36); recrystallization from ethyl acetate with a small amount of dichloromethane gives (3b). Yield: 0.40 g (8.0%). The other metal complexes, (3c), (3d), and (4b), were prepared by the same procedure as for (3b) except for the solvents of reaction and recrystallization (Table I). The purification of the complexes, (3c) and (3d), was carried out by column chromatography (silica gel, dichloromethane, *3c*: R_f = 0.80; *3d*: R_f = 0.95; *4b*: R_f = 0.36) and recrystallization.

Measurements

The final products were identified by elemental analysis using a Perkin Elmer Elemental Analyzer 240B, UV-VIS spectra using a Hitachi 330 spectrometer, and

^{1}H-NMR (250 MHz) (Brücker AC-250). The phase transition of the final compounds were observed with a polarizing microscope equipped with a heating plate controlled by a thermoregulator (Mettler FP80 and 82). The enthalpies of transition were measured with a differential scanning calorimeter (Rigaku Thermoflex TG-DSC). X-ray powder diffraction patterns were obtained with the Cu-Kα radiation using a Rigaku Geigerflex equipped with a hand-made heating plate controlled with a thermoregulator.[10]

RESULTS AND DISCUSSION

1. UV-VIS absorption spectra

The tetrapyrazinoporphyrazine derivatives are readily soluble in benzene, chloroform, dichloromethane and comparable solvents. The UV-visible absorption spectra are blue shifted as compared to the alkyloxymethyl-phthalocyanine derivatives[11] (Figure 2). No aggregation was observed. When the central metal of $(C_{12})_8PzM$ is changed in the order M = Cu → Ni → Co, the Q band is shifted to 634 nm → 627 nm → 616 nm, respectively (Table II). The absorption bands between the Q band and the soret band, which are attributed to dimers, are very weak.[12] Therefore, the long chain-substituted tetrapyrazinoporphyrazine derivatives do not form stable aggregates in chloroform solutions.

The absorption spectra of the cobalt (II) complex (3d) in pyridine and in chloroform were recorded. The intensity of the absorption band of the dimer was very strong in chloroform but very weak in pyridine. Pyridine must coordinate to the central metal in $(C_{12})_8PzCo$ leading to a dissociation of the aggregates.[13]

2. Effect of the central metal on the discotic mesomorphism of $(C_{12})_8PzM$ (M = 2H: 3a, Cu: 3b, Ni: 3c, Co: 3d)

All $(C_{12})_8PzM$ (M = 2H, Cu, Ni, Co) derivatives exhibit discotic columnar mesomorphism. The phase transition temperatures and enthalpy changes measured

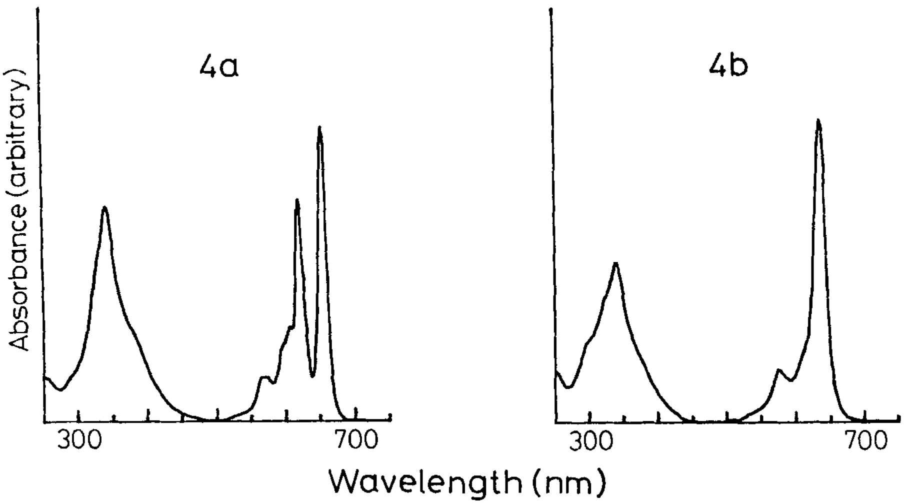


FIGURE 2 Electronic spectra of $(2\text{-EtC}_6)_8PzM$ (M = 2H, 4a; M = Cu: 4b) in $CHCl_3$.

TABLE II

Electronic spectra data of $(C_{12})_8PzM$ (M = 2H: 3a, Cu: 3b, Ni: 3c, Co: 3d) $(2\text{-}EtC_6)_8PzM$ (M = 2H: 4a, Cu: 4b) and $(2\text{-}EtC_6O)_8PcM$ (M = 2H: 5a, Cu: 5b)

Compound	Solvent	λ_{max} nm (log ϵ)
3a	$CHCl_3$	340(5.06) 564(4.38) 571(4.38) 605(4.72) 618(5.06) 654(5.18)
3b	$CHCl_3$	300(4.71)(sh) 340(4.99) 574(4.50) 634(5.25)
3c	$CHCl_3$	327(5.08) 356(4.65) 568(4.78) 602(4.53) 627(5.37)
3d	pyridine	340(5.02) 420(4.24) 566(4.40) 616(5.00)
4a	$CHCl_3$	343(5.08) 565(4.40) 572(4.41) 606(4.73) 620(5.10) 655(5.22)
4b	$CHCl_3$	340(5.00) 576(4.52) 636(5.27)
5a	CH_2Cl_2	346(5.06) 429(4.70) 601(4.54) 642(4.78)(sh) 662(5.23) 699(5.30)
5b	CH_2Cl_2	337(4.95) 420(4.56) 609(4.66) 646(4.65)(sh) 676(5.45)

The concentrations, in all cases, are in the range 10^{-5}-10^{-6}M.

by DSC and polarized light microscopy are summarized in Table III. The results of the powder X-ray diffraction of the mesophases are listed in Table IV.

2-1 Hexagonal disordered columnar mesophase (D_{hd}) in $(C_{12})_8PzH_2$ (3a)

When the crystals (K_1) of $(C_{12})_8PzH_2$ are heated for the first time from room temperature, they transform into K_2 crystals at 94°C and then into a mesophase at 118°C; on further heating, decomposition occurs at 238°C without clearing.

The mesophase was identified by X-ray diffraction at small angle. Two diffuse bands at 4.7 and 3.5 Å are observed corresponding to the molten alkyl chains and to the intracolumnar distance, respectively. Three narrow bands at 27.8, 16.1 and 13.6 Å are present in the small-angle region, which correspond to (100), (110) and (200) spacings in a two-dimensional hexagonal lattice (a = 32.2 Å).

The mesophase of $(C_{12})_8PzH_2$ (3a) can therefore be unambiguously assigned to belong to the hexagonal disordered columnar liquid crystals class.[14]

2-2 Rectangular disordered columnar (D_{rd}) in $(C_{12})_8PzM$ (M = Cu: 3b, Ni: 3c, Co: 3d) complexes

When $(C_{12})_8PzCu$ (3b) is heated, two crystal-to-crystal transitions are observed at 71°C and 92°C. Transformation into a mesophase occurs at 114°C and decomposition at 288°C without clearing. $(C_{12})_8PzNi$ has very similar behaviour (Table III). The cobalt complex does not exhibit such crystal polymorphism and the crystals

TABLE III

Transition temperatures (T_t) and enthalpy changes (ΔH_t) of $(C_{12})_8PzM$ (M = 2H: 3a, Cu: 3b, Ni: 3c, Co: 3d) and of $(C_{12})_8PcH_2$

	Phase $\dfrac{T_t/°C}{\Delta H_t/\text{Kcal.mol}^{-1}}$ Phase
$(C_{12})_8PzM$	
3a (2H)	$K_1 \xrightarrow[6.2]{94} K_2 \xrightarrow[8.8]{118} M \xrightarrow{238}$ Dec.
3b (Cu)	$K_1 \xrightarrow[4.9]{71} K_2 \xrightarrow[0.74]{92} K_3 \xrightarrow[10.2]{114} M \xrightarrow{288}$ Dec.
3c (Ni)	$K_1 \xrightarrow[1.8]{76} K_2 \xrightarrow[a]{98} K_3 \xrightarrow[7.7]{118} M \xrightarrow{264}$ Dec.
3d (Co)	$K \xrightarrow[3.5]{74} M \xrightarrow{255}$ Dec.
$(C_{12})_8PcH_2$ [b]	$K_1 \xrightarrow[14]{81} K_2 \xrightarrow[< 0.5]{120} M \xrightarrow[0.5]{252} I$

K : crystal ; M : mesophase ; I : isotropic liquid ; Dec. : decomposition

[a] This enthalpy change was too small to be determined

[b] from ref. 4

directly transform into a mesophase. In addition, the transition temperature from the crystal to the mesophase is remarkably lower than for the Cu and Ni complexes.

The mesophases were identified by small angle X-ray diffraction (Table IV). The X-ray diffraction pattern of $(C_{12})_8PzCu$ (3b) at 150°C is shown in Figure 3. This mesophase gives two diffuse bands at 4.7 and 3.4 Å, corresponding to the molten alkyl chains and to the interdisk-distance, respectively. It also gives five narrow bands at 28.9, 26.3, 16.4, 14.7 and 13.2 Å. In most cases, as for 3a, octasubstituted macrocyles give rise to two-dimensional hexagonal arrays of columns. In such a symmetry, the unit cell may be chosen in different ways (Figure 4A). Slight deformation of the arrangement yields other symmetries such as a centered rectangular lattice with two molecules per unit cell (Figure 4B). For the mesophases of 3b, 3c and 3d, the best agreement is obtained for a centered rectangular lattice with the parameters indicated in Table IV. There is a tilting angle between the plane of the macrocycles and the column axis in these mesophases; this differentiates them from 3a. In all cases, a diffuse halo around 3.4 Å was observed, indicating a disordered columnar mesophase (D_{rd}).

3. Mesomorphism of the 2-ethylhexyl-substituted macrocycles

2-Ethylhexyl derivatives are well known as plasticizers in polymer chemistry. This subunit has been previously used[6] to induce the formation of a nematic lenticular

TABLE IV

X-ray diffraction data of $(C_{12})_8PzM$ (M = 2H: 3a, Cu: 3b, Ni: 3c, Co: 3d)

Compound	Mesophase	Lattice constants (Å)	Spacing (Å)	Miller indices (hkl)
3a	D_{hd} at 150°C	a = 32.2	27.8	(100)
			16.1	(110)
			13.6	(200)
			ca. 4.7	-
			ca. 3.5	-
3b	D_{rd}(C2/m) at 150°C	a = 57.7 b = 29.6	28.9	(200)
			26.3	(110)
			16.4	(310)
			14.7	(020)
			13.2	(220)
			ca. 4.7	-
			ca. 3.4	-
3c	D_{rd}(C2/m) at 150°C	a = 54.8 b = 28.5	27.4	(200)
			25.3	(110)
			15.8	(310)
			14.3	(020)
			12.9	(220)
			ca. 4.7	-
			ca. 3.4	-
3d	D_{rd}(C2/m) at 150°C	a = 54.8 b = 29.1	27.4	(200)
			25.7	(110)
			15.7	(310)
			14.5	(020)
			12.8	(220)
			ca. 4.7	-
			ca. 3.4	-

mesophase. In all cases, the transition temperatures to the isotropic phases are significantly decreased (Table V). For most compounds, two different mesophases can be identified. In the pyrazine series, the enthalpy of transition for the mesophase to isotropic liquid is larger than the K → M_1 and $M_1 \rightarrow M_2$ enthalpies. The mesophase is therefore still highly organized. In the case of phthalocyanine derivatives, the high temperature phase is nematic; the enthalpy of transition to the isotropic liquid is correlatively small and the largest enthalpy corresponds to the $M_1 \rightarrow M_2$ transition.

The X-ray diffraction patterns may be assigned by assuming a simplified polyominoes shape for the molecule (Figure 5). The polyominoes model has been previously reported.[15] The 2-ethylhexyloxy-phthalocyanine may be approximated by a square of 23 × 23 Å^2. In the mesophase, the squares pile up to form a tetragonal arrangement in the case of the metal free derivatives (Figure 6A and Table VI). A halo around 4.7 Å indicates the coherence length of the paraffinic side chains. The microstructure observed by crossed polarized light microscopy for $(2\text{-EtC}_6)_8PzH_2$ (Figure 7) (M_2 mesophase) is very similar to the one observed for substituted phthalocyanines (M_1 mesophase). In the case of the copper complex $(2\text{-EtC}_6O)_8PcCu$, a drastic change in the X-ray patterns is obtained as compared

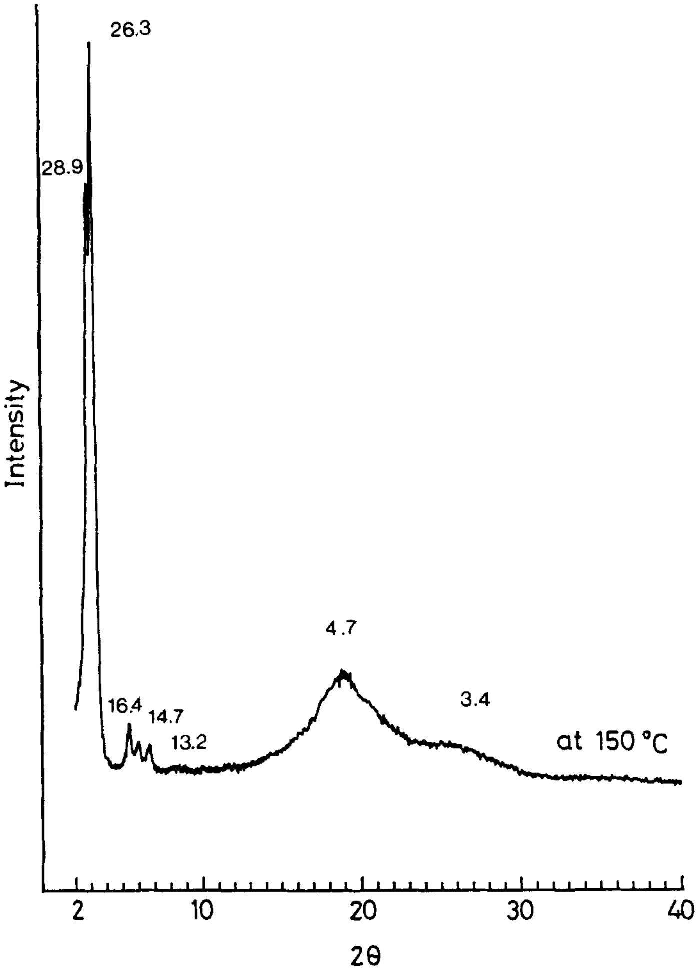


FIGURE 3 X-ray diffraction pattern of $(C_{12})_8$PzCu at 150°C. The values (in Å) corresponding to the peaks are indicated on the figure.

to the metal free derivative. It can be explained by assuming a small deformation of the tetragonal lattice (Figure 6B). This deformation is very probably due, as previously, to the appearance of a tilting angle between the plane of the macrocycle and the axis of the column. This phenomenon must be favoured by the strong tendency of the copper complexes to bind ligands in the axial position.

$(2\text{-EtC}_6)_8$PzCu also forms a mesophase with a diffuse band around 4.7 Å. However no simple assignment of the X-ray pattern could be made. The low temperature mesophase (M_1) of $(2\text{-EtC}_6)_8\text{PzH}_2$ is still highly organized and approximately corresponds to a D_r symmetry with two molecules per unit cell. As previously, no further assignment could be made.

4. Redox properties

The redox properties of $(C_{12})_8$PzM (M = 2H, Cu, Ni) and of $(2\text{-EtC}_6\text{O})_8$PcM (M = 2H, Zn) have been determined by cyclic voltammetry in CH_2Cl_2 (Table VII).

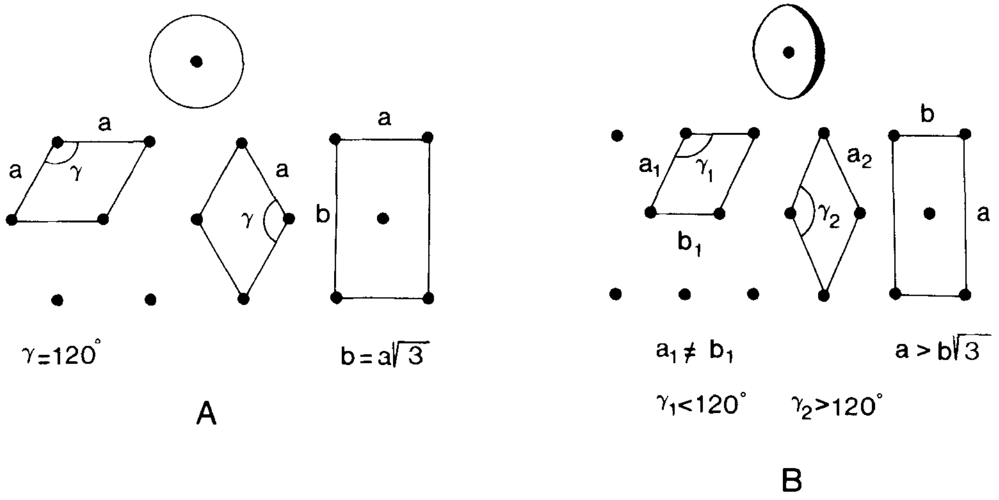


FIGURE 4 A: Some of the ways of taking the unit cell in a ^{2}D hexagonal array. B: The transformation of the hexagonal symmetry into a centered rectangular lattice (C2/m) when the macrocyles form a tilting angle with the axis of the columns. In table IV only the a, b parameter are listed. At the top of the figure, the polyominoe representation of the molecular unit is given.

TABLE V

Transition temperatures (T_t) and enthalpy changes (ΔH_t) of 2-Ethylhexyl substituted macrocyles

	Phase	$\xrightarrow[\Delta H_t/\mathrm{Kcal.mol^{-1}}]{T_t/^\circ C}$	Phase		Phase		Phase
$(2\text{-Et-}C_6)_8$PzM							
4a (2H)*	K	$\xrightarrow[0.95]{74\text{-}81}$	M_1	$\xrightarrow[0.31]{193}$	M_2	$\xrightarrow[4.3]{219}$	I
4b (Cu)	K	$\xrightarrow[2.8]{ca.90}$	M	$\xrightarrow[7.5]{232}$			I
$(2\text{-EtC}_6\text{O})_8$PcM							
5a (2H)§	K	$\xrightarrow[1.1]{170}$	M_1	$\xrightarrow[1.82]{223}$	M_2	$\xrightarrow[0.78]{270}$	I
5b (Cu)	K	$\xrightarrow[0.2]{204}$	M_1	$\xrightarrow[2.3]{242}$	M_2	$\xrightarrow[1.1]{290}$	I

---

*The melting point of this depends on the thermal history of the sample.

§ from ref. 6. Same legend as in Table 3.

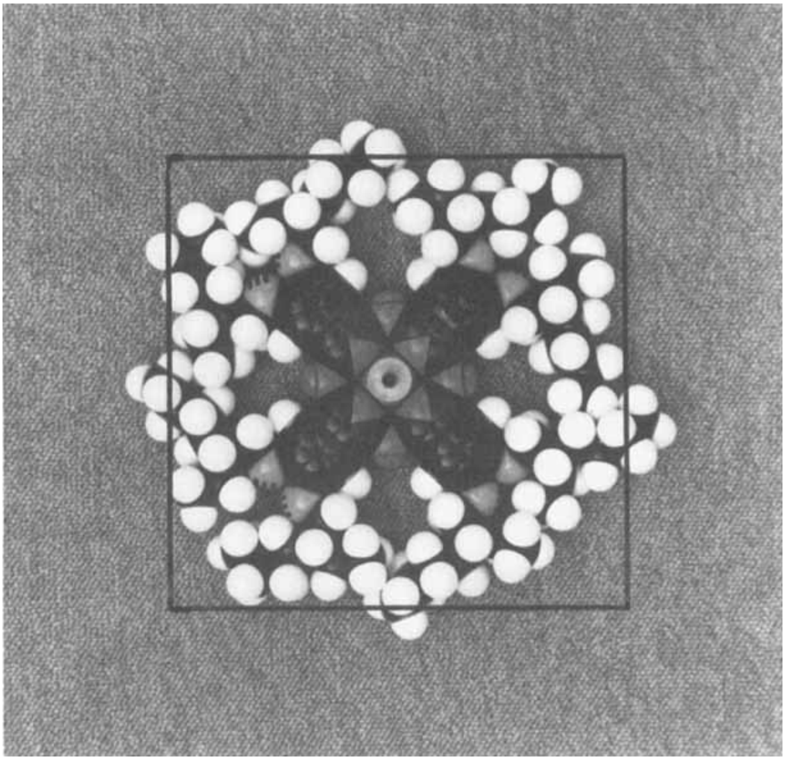


FIGURE 5 CPK molecular model of $(2\text{-}EtC_6O)_8PcH_2$ and its polyominoes representation (for polyominoes model see reference 15). See Color Plate I.

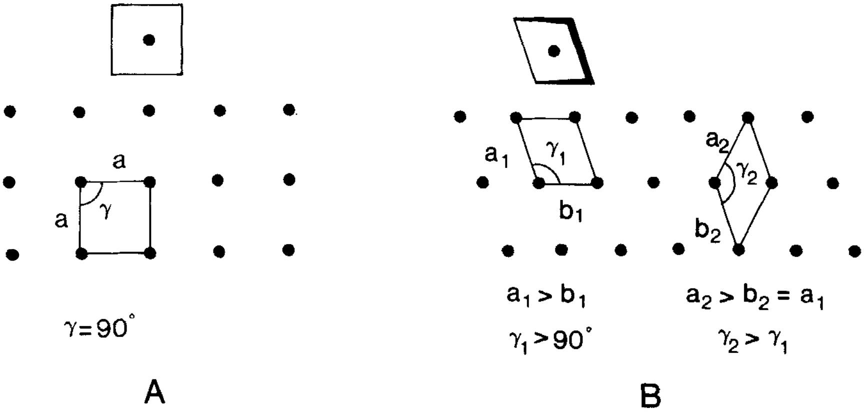


FIGURE 6 Schematic representation of the ^2D lattices obtained for 2-Ethylhexyl substituted macrocycles. A: tetragonal, B: oblique.

The use of pyrazine moieties increases by approximately 0.5 V the reduction potential of the pyrazinoporphyrazine derivatives as compared to the phthalocyanine ones. Reduction involves the π^* orbitals of the aromatic rings; the formation of

TABLE VI

X-ray diffraction data of the 2-ethylhexyl-substituted macrocycles

Compound	Mesophase	Spacing (Å)	Miller indices
$(2\text{-}EtC_6)_8PzH_2$			
4a	M_1		
D_r	a = 35.0	17.5	(200)
at 140°C	b = 17.1	15.4	(110)
		12.7	(210)
		10.3	
		7.8	(220)
		5.3	
		5.0	
		ca. 4.7	-
Tetragonal	M_2		
at 200°C	a = 21.3	21.3	(100)
		15.8	(110)
		10.5	(200)
		7.4	(220)
		ca. 4.7	-
$(2\text{-}Et\ C_6O)_8PcM$			
5a (2H)			
Tetragonal	M_1	23.3	(100)
	a = 23.3	16.6	(110)
		11.6	(200)
		8.4	(220)
5b (Cu)			
M_1			
Oblique	a = 23.1	22.49	(100)
	b = 18.9	18.42	(010)
	γ = 103°	16.13	(-110)
		13.06	(110)
		8.74	(210)
		7.96	(120)

the corresponding metal complexes therefore changes the reduction potentials by only 0.1 eV as compared to the metal free derivative.

The oxidation potential of phthalocyanine derivatives substituted with alkyloxy groups is around +0.5 V. Therefore, mixed columnar liquid crystals of s-PzH_2 and s-PcM should demonstrate a significant charge transfer between the molecular units.

Conclusion

New types of discogens based on tetrapyrazinoporphyrazine derivatives have been synthesized. They form rectangular columnar liquid crystals in the case of $(C_{12})_8PzM$ and their liquid crystalline properties are very similar to those of their phthalocyanine homologues. Tetrapyrazinoporphyrazines are more easily reduced than the corresponding phthalocyanines and they can be used as electron acceptors in mixed columnar liquid crystals. The pyrazine moieties can also be used to form metal complexes or they can be transformed into the pyrazinium derivatives by methylation. Such studies are in progress.

TABLE VII

Reduction potentials of $(C_{12})_8PzM$ and $(2\text{-}EtC_6O)_8PcM$ (in V vs SCE in CH_2Cl_2)

Compound	$\Delta E^{1/2}_{red}$	$\Delta E^{1/2}_{ox}$
$(C_{12})_8PzM$		
3a (2H)	-0.41	
3b (Cu)	-0.55	
3c (Ni)	-0.55	
$(2\text{-}EtC_6O)_8PcM$		
5a (2H)	-0.94	+0.6
5c (Zn)	-1.05	+0.5

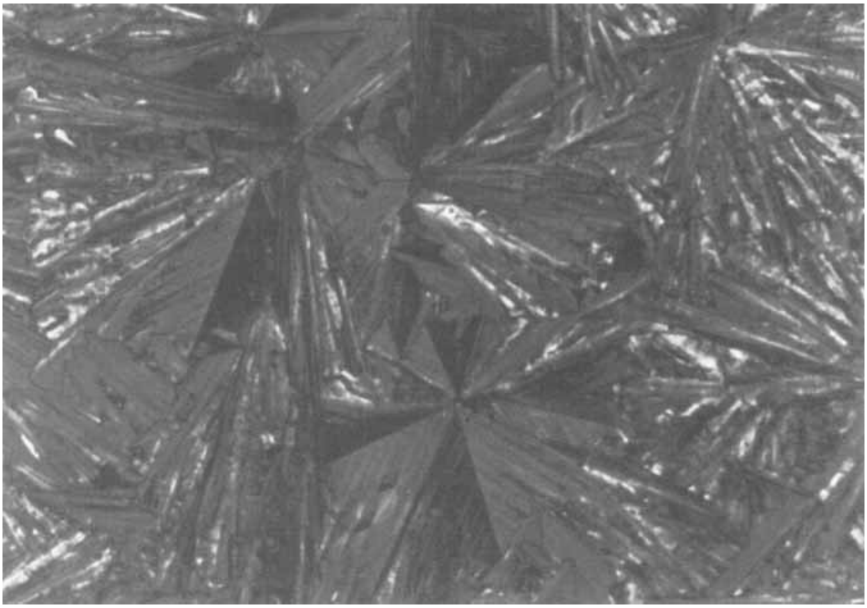


FIGURE 7 Microstructure observed by crossed polarizer optical microscopy for $(2\text{-}EtC_6)_8PzH_2$ at 210°C (M_2 mesophase). See Color Plate II.

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