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Light absorption and hole-transport properties of copper corroles: from aggregates to a liquid crystal mesophase.

Di Gao,¹ Judicaelle Andeme Edzang,² Abdou Karim Diallo,² Thibault Dutronc,³ Teodor Silviu Balaban,⁴ Christine Videlot-Ackermann,⁺⁵ Emmanuel Terazzi⁺ and Gabriel Canard⁺

The synthesis of the corrole-based liquid crystal phase CorLC is described together with its full characterization by a combination of Polarised Optical Microscopy (POM), ThermoGravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) measurements and Small-Angle X-Ray Diffraction (SA-XRD) which shows that CorLC has an hexagonal columnar organization at room temperature. The light absorption and hole-transport properties of the mesophase CorLC is compared with the ones featured by assemblies of its parent meso triaryl (Cor1) and per-aryl (Cor2) derivatives. J-Aggregates are changed into H-aggregates when the intermolecular distance is increasing with the peripheral steric hindrance producing lower hole-transport properties.

Introduction

The highly versatile optical, electronic and photophysical properties of porphyrin and phthalocyanine derivatives has led to their large application in the fields of organic electronics and optoelectronics.¹ In this regard, their ability to produce large assemblies or aggregates is particularly employed to construct organized and high light-absorbing materials displaying efficient charge and/or exciton transport properties that are essential in the preparation of organic solar cells² or photoconductors.³ Among the different supramolecular tools that are used to build self-organized porphyrin and phthalocyanine systems, their incorporation in liquid crystal (LC) phases⁴ is attractive since the morphology and orientation of LC thin films can be controlled to obtain large area and defect free devices.⁵ For example, an exciton diffusion length longer than 12 nm has been measured in a nematically organized porphyrin layer⁶ while a field-effect mobility of 0.7 cm² V⁻¹ s⁻¹ was exhibited by an Organic Field Effect Transistor (OFET) incorporating a liquid crystalline copper phthalocyanine.⁷

Corrole and its metal complexes are currently attractive members of the porphyrinoid family since their syntheses⁸ and functionalizations⁹ have been extensively developed during the last fifteen years and are thus amenable to gram-scale synthesis, sometimes essential for developing devices. Consequently, corrole derivatives are employed in many research areas including catalysis,¹⁰ sensors¹¹ or medicine.¹² Nevertheless, very few reports concern the preparation and characterization of large corrole-based assemblies¹³ and their incorporation into electronic devices.¹⁴ We report here the synthesis and full characterization of a copper corrole-based liquid crystal mesophase CorLC (Scheme 1). Its supramolecular organization was studied by UV/Visible spectroscopy and was compared to the ones produced by aggregates of its parent meso triaryl (Cor1) and per-aryl (Cor2) derivatives (Scheme 1). The hole-transport properties of these three compounds were additionally measured through their incorporation in OFETs.

Results and discussion

Synthesis of the mesogen CorLC.

The liquid crystal CorLC was prepared in four synthetic steps starting from the copper(III) meso-tris(p-methoxyphenyl)corrole Cor1 (Schemes 1 and S1, ESI†).¹⁵ The full bromination of β-positions followed by a Suzuki cross-coupling procedure afforded the per-aryl substituted copper corrole Cor2 as previously reported.¹⁶ A demethylation using standard conditions afforded the per-aryl complex substituted by eleven p-hydroxyphenyl groups in 44% yield without any noticeable removal of the copper ion. It has to be noted that this latter derivative is enough soluble in sufficiently polar media in order to be purified and characterized. The expected compound CorLC was prepared in a yield of 23% by the subsequent condensation of an excess of the benzyl chloride derivative 1 in basic conditions. Its purity was confirmed by its ¹H NMR spectrum and by its MALDI-TOF spectrum showing only its molecular peaks and the corresponding sodium adduct (ESI†). We note here that if a reaction has to be performed more than tenfold on the same substrate, without allosteric effects, it is remarkable that the overall yield is in the two digit region.
2

transition (-30 °C, transformed to the Col phase characterized by a fan texture that strongly suggests that at very low speed (0.1 °C∙min⁻¹) at room temperature. Cooling down the isotropic liquid sample

Notably, the liquid crystal phase remains birefringent and fluid reversible and occurs at 95 °C (i.e. with a small hysteresis). A standard liquid state (I). Upon cooling, this phase transition is

a liquid-crystalline organization. This texture does not show any significant changes until the isotropisation occuring at 30 °C (Fig. S1, ESIF). Temperature dependent POM observations showed a fluid and birefringent texture that is typical of the occurrence of a liquid-crystalline organization. This texture does not show any significant changes until the isotropisation occurring at 103 °C i.e. a transition from the liquid crystalline phase to the standard liquid state (I). Upon cooling, this phase transition is reversible and occurs at 95 °C (i.e. with a small hysteresis). Notably, the liquid crystal phase remains birefringent and fluid at room temperature. Cooling down the isotropic liquid sample at very low speed (0.1 °C·min⁻¹) forms the liquid crystalline phase characterized by a fan texture that strongly suggests that the compound self-organizes in a columnar hexagonal (Colh) liquid crystalline phase (Fig. 1a). This preliminary result was confirmed by DSC (Fig. 1b). The solid complex CorLC was transformed to the Colh mesophase through a broad first order transition (-30 °C, ΔH = 80.4 kJ·mol⁻¹, ΔS = 330.5 J·mol⁻¹·K⁻¹) that preceded a second first order transition (103.4 °C, ΔH = 22.1 kJ·mol⁻¹, ΔS = 58.8 J·mol⁻¹·K⁻¹) of the Colh phase into the liquid isotropic state I.

**Scheme 1** Synthesis of the liquid crystal corrole CorLC. i) a) Br₂, pyridine, CHCl₃; b) Na₂S₂O₅, H₂O (45%). ii) Pd₃(dbta)₆, K₂CO₃, p-H₂CO-C₆H₄-B(OH)₂, toluene (71%). iii) BBr₃, CH₂Cl₂ (44%). iv) K₂CO₃, DMF (23%).

**Thermal behaviour of CorLC.**

The thermal behavior of CorLC was studied by a combination of Polarisé Optical Microscopy (POM), ThermoGravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) measurements and Small-Angle X-Ray Diffraction (SA-XRD) (Fig. 1, Fig. S1, S2 and S3, ESIF). The TGA measurement indicates that the compound is stable up to 300 °C (Fig. S1, ESIF). Temperature dependent POM observations showed a fluid and birefringent texture that is typical of the occurrence of a liquid-crystalline organization. This texture does not show any significant changes until the isotropisation occurring at 103 °C i.e. a transition from the liquid crystalline phase to the standard liquid state (I). Upon cooling, this phase transition is reversible and occurs at 95 °C (i.e. with a small hysteresis). Notably, the liquid crystal phase remains birefringent and fluid at room temperature. Cooling down the isotropic liquid sample at very low speed (0.1 °C·min⁻¹) forms the liquid crystalline phase characterized by a fan texture that strongly suggests that the compound self-organizes in a columnar hexagonal (Colh) liquid crystalline phase (Fig. 1a). This preliminary result was confirmed by DSC (Fig. 1b). The solid complex CorLC was transformed to the Colh mesophase through a broad first order transition (-30 °C, ΔH = 80.4 kJ·mol⁻¹, ΔS = 330.5 J·mol⁻¹·K⁻¹) that preceded a second first order transition (103.4 °C, ΔH = 22.1 kJ·mol⁻¹, ΔS = 58.8 J·mol⁻¹·K⁻¹) of the Colh phase into the liquid isotropic state I.

**Fig. 1** (a) Optical texture observed by the POM of CorLC in the Colh mesophase at 90 °C after cooling from the isotropic liquid. (b) DSC trace of CorLC recorded at 5 °C/min (second heating and cooling). (c) SA-XRD profile in the liquid crystalline phase and associated indexation of CorLC at 30 °C.

**Structure of the CorLC mesophase.**

Temperature-dependent SA-XRD patterns of CorLC were recorded in the 20-140 °C temperature range. The presence of a large and diffuse signal at approximately 4.5 Å (h₃₃), which was associated with the liquid-like molten chains confirmed the fluid-like nature of the mesophase. Short acquisition times (i.e.
Aggregation properties of Cor1, Cor2 and CorLC.

Copper meso-triarylcorroles are known to show hyper electronic spectra that are strongly sensitive to the nature of the meso-substituents that are involved in phenyl-to-Cu($d_{x^2-y^2}$) charge transfers and contribute to the main Soret band peak. This orbital interaction is due to and increases with the saddling of the macrocycle which is reinforced by the introduction of bulky aryl groups.

Electron-donating properties of these two groups and shows that the concomitant introduction of 11 additional aryl groups and 21 peripheral alkyl chains does not produce any supplementary distortion of the aromatic corrole ring.

Thin solid films of Cor1, Cor2 and CorLC were prepared by the slow evaporation of their respective dichloromethane solutions. The formation of aggregates is illustrated by the broadening of the resulting electronic spectra that gives, in addition, insights of the relationship between the corroles substitutions and their supramolecular organizations (Fig. 2).

Fig. 2 Normalized UV-Visible absorption of diluted dichloromethane solutions (dashed lines) and thin solid films (solid lines) of Cor1, Cor2 and CorLC.

The band maxima are red-shifted by ca 15 nm when assemblies of Cor1 are produced because of the probable formation of J-
aggregates. This supramolecular architecture is commonly observed in the single crystal X-ray structures of copper meso-triarylcorrole derivatives where corrole assemblies are formed thanks to, among others, an intermolecular interaction between the meso-aryl group of one complex with the metallic centre of the adjacent one producing short inter-macromolecule distances.

On the other side, the per-aryl substitution of Cor2 and CorLC induces the formation of H-aggregates as evidenced by the ca 20 nm blue-shift of their Soret band maxima (Fig. 2). The peripheral sterical hindrance of Cor2 combined with the multiple intermolecular interactions between alkyl chains in the LC phase CorLC inhibits the direct participation of the copper ion in the supramolecular organization and thereby allows the formation of a different intermolecular packing. The formation of H-assemblies along the column axis is in accordance with the Col\(\alpha\) organization of the CorLC mesophase (see below).

**Hole-transport properties of Cor1 and Cor2.**

To further study the physico-chemical properties of Cor1, Cor2 and CorLC assemblies, their charge-transport properties were investigated through their incorporation in OFETs. Bottom-gate thin-film transistors with bottom electrode contacts were fabricated to realize so-called BGBC (Bottom-Gate Bottom-Contact) devices. Linear channel lengths (L = 25 or 50 \(\mu\)m) were realized by vacuum evaporation of gold through a shadow mask directly on the gate. To complete the device structure, the depositions of the active layers were achieved by drop-casting of dichloromethane solutions (or liquid CorLC) onto the surface of linear BGBC devices. All measurements were performed in air and at room temperature. Even if numerous OFETs were prepared for each derivative, only the two best results obtained among the operating transistors are presented herein.

A field effect transistor activity was observed for Cor1 and Cor2-based assemblies by applying a negative drain and negative gate voltages in order to operate in the accumulation mode. These results demonstrate that Cor1 and Cor2 behave as p-type semiconductors in air as shown by the typical output characteristics of a Cor1-based OFET on Si/SiO\(\text{2}\) substrate under negative and positive voltages (Fig. 3a and Fig. 3b). Under negative gate voltages, the successive increase of the drain current indicates that the BGBC device based on Cor1 operates as an accumulation mode p-channel device (Fig. 3a). The transport of positive carriers is confirmed by the depletion mode under positive voltages (Fig. 3b). In the depletion mode, carriers are driven away from the semiconductor interface, which leads to a decrease of the drain current. The field effect mobility (\(\mu\)), threshold voltage (\(V_T\)) and on/off ratio (\(I_{on}/I_{off}\)) of the most efficient OFETs incorporating Cor1 and Cor2 are summarized in Table 1 (All results are presented in Table S1, ES\(\text{F}\)). The highest field effect mobility in the saturation regime at \(V_D = -90 V\) was extracted for Cor1 and gives a value of \(1.36 \times 10^{-5} cm^2/V.s\) together with a threshold voltage \(V_T\) of +14.8 V and an on/off ratio of 24.5. The increasing sterical hindrance of the peripheral substitution of Cor2 probably produces a lower mobility of \(1.32 \times 10^{-5} cm^2/V.s\) together with a threshold voltage \(V_T\) of +38.5 V and an on/off ratio of 10. All devices incorporating CorLC failed to give charge-transport properties. Identical results were obtained when an hydrophobic substrate Si/SiO\(\text{2}\) modified by a grafted self-assembly monolayer of long alkyl chains was used to induce the homeotropic alignment of the CorLC discotic molecules. Even though thin films were cast as such, or with an annealing step, these failed to improve the microstructural order for achieving more efficient charge transport properties in Cor1, Cor2 and CorLC thin films. However, these functional transistors are the first examples of OFETs using corrole derivatives as active layers and the variation of their low efficiencies are still illustrating the impact of the peripheral substitution on the corroles supramolecular organization.

**Table 1:** Field effect mobilities (\(\mu\)), threshold voltages (VT) and on/off ratio (\(I_{on}/I_{off}\)) of corrole-based OTFT devices.

<table>
<thead>
<tr>
<th></th>
<th>(\mu) ((cm^2/V.s))</th>
<th>(V_T) (V)</th>
<th>(I_{on}/I_{off})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cor1</td>
<td>(1.36 \times 10^{-5})</td>
<td>+14.8</td>
<td>24.5</td>
</tr>
<tr>
<td>Cor2</td>
<td>(1.32 \times 10^{-5})</td>
<td>+38.5</td>
<td>-10</td>
</tr>
</tbody>
</table>

**Conclusions**

We described herein the synthesis and full characterization of the first example of a corrole-based liquid crystal mesophase (CorLC). This mesophase features, at room temperature, an hexagonal columnar organization combined with an H-arrangement of the discotic chromophores producing a blue shifted light absorption. This study shows that the introduction of numerous peripheral groups on copper corroles tunes their aggregation modes and their hole-transport properties. Since the copper ion can be removed using mild experimental conditions, CorLC can be used to prepare liquid crystal phases incorporating other metallic centers such as Co(III)\(^{13}\) and Mn(III)\(^{14}\) that are already applied in the fields of sensors.
Experimental section

General Remarks

All reagents were purchased from Acros, Alfa Aesar or Aldrich and were used without further purification unless otherwise stated. Toluene was distilled from sodium and benzophenone. Dichloromethane, hexane and n-heptane were distilled from calcium hydride. Dichloromethane stabilized by methanol was used during the preparation of OFETs. SiO₂ gel plates Merck 60 F254 were used for Thin Layer Chromatography (TLC). SiO₂ gel 60 (230-400 mesh) was used for preparative column chromatography. Flash column chromatography was performed on silica gel 60 (230-400 mesh). (3,5-bis(dodecyloxy)phenyl)methanol, Cor1 and Cor2 were prepared and purified according to literature procedure.

Spectroscopic and analytical measurements

1H Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 400 Ultrashield NMR spectrometer. Chemical shifts are given in ppm relative to residual peaks of chloroform (δ = 7.26 ppm). DMSO-d₆ (δ = 2.50 ppm) or THF-d₈ (δ = 1.73 and 3.58 ppm).

UV/Vis absorption spectra were measured with a Shimadzu UV-2401 (PC) instrument or with a Varian Cary 1E spectrophotometer.

Pneumatically-assisted electrospray (ESI-MS) mass spectra were recorded from 10-4 M solutions on an Applied Biosystems API 150EX LC/MS System equipped with a Turbo Ionspray source and were used within the positive ion mode (Waters) spectrometer. These two instruments are equipped with a high pressure (200 bar) nebulizer. The on-off ratio values were determined from the i-V transfer plots under a constant drain-source voltage VD = -100 V.

Organic syntheses.

Compound 1: (3,5-bis(dodecyloxy)phenyl)methanol (5.00 g, 10.5 mmol) was dissolved in dry CH₂Cl₂ (50 mL) and DMF (50 μL) was added under a nitrogen atmosphere. A solution of SOCl₂ (1.87 g, 15.7 mmol) in dry CH₂Cl₂ (50 mL) was added dropwise over a period of 1 h and then stirred at room temperature for 4 days. The reaction mixture was stirred at room temperature for 24 h, evaporated to dryness and dried under vacuum to afford 1 as a white solid (5.15 g, 94.5%). CI = 357.4; calcd for C₄₃H₇₉NO₂: m/z: (M+): 615.4. The crude compound was precipitated by pouring the reaction mixture into water (100 mL). The precipitates were filtered and purified by chromatography on silica gel (CH₂Cl₂/MeOH 9:1) to afford 2 as a white solid (4.97 g, 83.4%).

CuIII undeca-(4-hydroxyphenyl)corrole: A 1M solution of BBr₃ in CH₂Cl₂ (10 mL, 10 mmol) was added to a solution of Cor2 (45 mg, 29.6 μmol) in CH₂Cl₂ (6 mL) which was stirred at 0 °C for 15 min. The mixture was kept at 0 °C for 1 h and then stirred at room temperature for 3 days before CH₂Cl₂ (20 mL) and CH₃OH (10 mL) were added together with an aqueous saturated solution of NaHCO₃ (35 mL). The crude compound was precipitated by pouring the reaction mixture into water (100 mL). The precipitates were filtered and purified by chromatography on silica gel (CH₂Cl₂/MeOH, 5:1) to afford 3 as a brown powder (18 mg, 13.1 μmol, 44%). Rf = 0.11 (CH₂Cl₂/CH₃OH, 4:1). 1H NMR (400 MHz, THF-d₈, 25 °C): δ = 8.78 (s, 2H, Ar-CHO), 7.93 (s, 3H, Ar-OH), 7.53 (s, 2H, Ar-CHO), 7.47 (s, 2H, Ar-OH), 6.94 (d, 3J(H, H) = 8.4 Hz, 2H, Ar-H), 6.76 (d, 3J(H, H) = 7.9 Hz, 4H, Ar-H), 6.66 (d, 3J(H, H) = 8.4 Hz, 4H, Ar-H), 6.40 (d, 3J(H, H) = 7.6 Hz, 8H, Ar-H), 6.40 (d, 3J(H, H) = 8.0 Hz, 4H, Ar-H), 6.27 (d, 3J(H, H) = 8.5 Hz, 4H, Ar-H), 6.09 (m, 8H, Ar-H). 3J(H, H) = 8.6 Hz, 4H, Ar-H), 5.96 (d, 3J(H, H) = 7.5 Hz, 4H, Ar-H), 5.93 ppm (d, 3J(H, H) = 8.5 Hz, 2H, Ar-H). UV-Vis (THF): λmax (ε × 10⁻³) = 468 (83.6), 550 (18.7), 643 nm (12.2). MALDI-TOF (M⁺): 1372.0; calcd for Cu₃H₇₁Cu₂N₇O₁₃: 1373.0.

OFET preparations and studies

Cor1, Cor2 and CorLC were dissolved in CH₂Cl₂ to a concentration of ca 5.10⁻¹⁰ M. The Bottom-Gate Bottom-Contact (BGBC) configuration was used for the OTFT devices. Highly n-doped silicon wafers (gate), covered with thermally grown silicon oxide SiO₂ (3000 Å, insulator layer), were purchased from Vegatec (France) and used as bottom-gate substrates. The capacitance per unit area of silicon dioxide dielectric layers was 1.2×10⁻⁵ F/cm². The gold (Au) source and drain electrodes (channel length L = 25 or 50 μm, channel width W = 1 mm) were evaporated directly on SiO₂ layer prior the organic deposition through a shadow mask. Solutions of Cor1, Cor2 and CorLC (or pure liquid CorLC) were deposited by drop-casting to form the organic active layers in OTFT devices through a dropwise addition of 20-40 μL volumes onto the devices surfaces. Such volume covered entirely the channel of one OTFT and beyond. After the organic solution deposition, the devices were left overnight in ambient condition in order to remove residual solvent prior electrical measurements. A post-annealing step from 50 to 80°C was applied to all devices in order to increase the microstructural order of thin films. Current-voltage characteristics were recorded at room temperature under ambient conditions with Hewlett-Packard 4140B, or 4145A, pico-ammeter-DV source. The source-drain current (ID) in the saturation regime is governed by the equation (2):

(2) (Iₒ/2)= (W/2L) Cᵢ(Vₒ-Vᵢ)²

where Ci is the capacitance per unit area of the gate insulator layer, VG is the gate voltage, VT is the threshold voltage, and μ is the field-effect mobility.

CorLC: CuIII undeca-(4-hydroxyphenyl)corrole (7.2 μmol, 10 mg), compound 1 (22 equiv., 79.2 μmol, 39 mg) and K₂CO₃ (44 equiv., 158.4 μmol, 22 mg) were added to a round-bottomed flask which was oven dried overnight at 111 °C. The flask was evacuated and backfilled with argon three consecutive times. Dry DMF (5 mL) was then charged by a syringe. The mixture was subsequently stirred at 90 °C for 24 h. After being cooled to room temperature, the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on silica gel.
Acknowledgements
Dr. Laure Guénée is acknowledged for SA-XRD measurements. Dr. Di Gao gratefully thanks the China Scholarship Council for granting him his PhD fellowship in Marseille.

Notes and references

**a** Tariel Mesiano, Olivier Lodeiro, J. F. B. Barata, S. M. Santos, M. A. F. Faustino, J. A. S. Cavaleiro and T. Trindade, **J. Porphyrins Phthalocyanines**, 2015, 19, 1811.


