

# Liquid crystalline octaalkoxycarbonyl phthalocyanines: design, synthesis, electronic structure, self-aggregation and mesomorphism†

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We describe a practical synthesis of octaalkoxycarbonyl phthalocyanines that are well soluble in various organic solvents and form liquid crystalline columnar mesophases at room temperature. The ground-state geometry, HOMO/LUMO energies, vertical transition energies and the corresponding oscillator strengths have been calculated for the isolated molecules. The redox behavior of octaalkoxycarbonyl phthalocyanines was investigated by cyclic voltammetry and their aggregation in solution by <sup>1</sup>H NMR spectroscopy. The supramolecular structure of the liquid crystalline mesophase of a novel phthalocyanine bearing branched alkyl chains was studied by powder X-ray diffraction. The length and branching of peripheral alkyl chains are found to be two structural parameters affecting the formation of mesophases and self-aggregation in solution.

## Introduction

Disk-like mesogens, typically comprising a flat rigid aromatic core substituted with relatively long and flexible peripheral chains, have been attracting considerable interest in recent years. Due to the cofacial stacking of aromatic cores, disk-like molecules self-organize into one-dimensional columnar “supramolecular wires”, with the peripheral substituents acting as “insulators”. The transport along the axis of columnar stacks in discotic mesophases is thus much faster than between columns.<sup>1</sup> Due to their relatively high charge carrier mobilities and tendency to form highly ordered films of various thicknesses, discotic mesogens have been considered as attractive candidates for application in organic electronic devices such as photovoltaic solar cells, light emitting diodes (LEDs) and field effect transistors (FETs).<sup>2</sup>

However, besides appropriate electronic properties, the morphology of the material is of key importance for device performance. In particular, it is crucial to align the molecules in a gap between the electrodes in order to create a defect-free pathway for efficient charge transport. This can be achieved by processing techniques such as zone-casting from solution or by thermal processing. For successful processing from solution materials should obviously be well soluble in organic solvents. In addition, it has been recently demonstrated that fabrication of ordered thin films by zone-casting is strongly affected by aggregation in solution.<sup>3</sup> On the other hand, melt processing

techniques require adequate temperatures of transition between liquid crystalline and isotropic phases to avoid thermal decomposition of materials or substrates.

Phthalocyanines have found a few important practical applications as dyes and pigments due to their strong absorption of light combined with extraordinary thermal and photostability.<sup>4</sup> In addition, they have been investigated for their potential use in many other fields, including catalysis, chemical sensors, non-linear optical materials, ink-jet printing, electrophotography, and photodynamic therapy.<sup>5</sup> Phthalocyanine-based disk-like mesogens have also been widely investigated for applications in electronic devices.<sup>6</sup> High charge carrier mobility (up to 0.2 cm<sup>-2</sup> V<sup>-1</sup> s<sup>-1</sup>) in the columnar phases of the liquid crystalline octaalkyl phthalocyanine has been recently reported.<sup>7</sup>

As is the case for other disk-like molecules, the control of morphology in thin films is also a crucial issue in phthalocyanine-based materials. Since, up to now, most studies show that phthalocyanines act as p-type (hole transporting) semiconductors,<sup>7,8</sup> our intention is to design phthalocyanine mesogens combining n-type (electron transporting) behavior with good processability both by solution methods and by thermal annealing. Here, we report the synthesis and studies of octa-substituted phthalocyanines **1a–e** designed as n-type semiconducting discotic mesogens.

## Results and discussion

### Design

We have reported in a previous study the synthesis and characterization of tetraalkoxy-substituted phthalocyanines designed as p-type liquid-crystalline semiconductors.<sup>9</sup> It is known that n-type behavior is observed with electron-deficient systems.<sup>10</sup> In order to induce n-type semiconductivity, we decided to introduce eight electron-withdrawing alkoxy-carbonyl groups (COOR, R = alkyl) in the *peripheral* positions of the phthalocyanine core.<sup>11</sup> Adjacent alkoxy-carbonyl groups

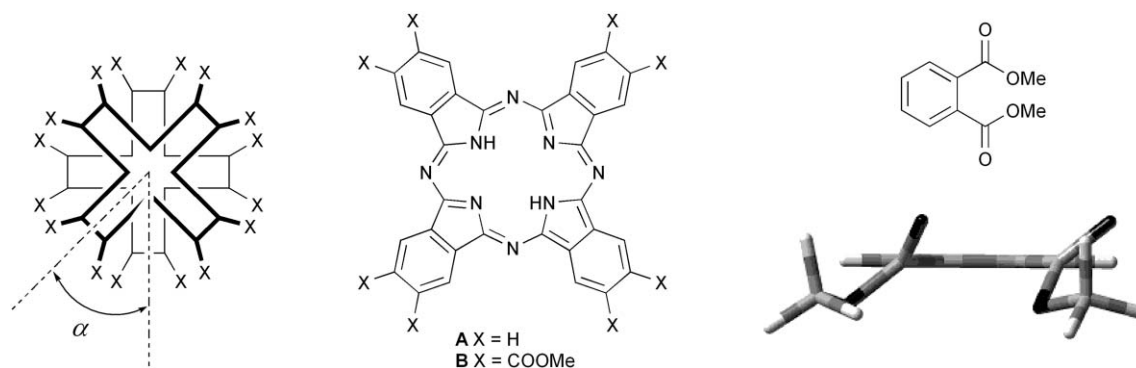
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† Electronic supplementary information (ESI) available: synthetic details and analytical data for **1a,b,d,e**, **2** and **3**; powder X-ray diffraction data and POM image of **1c**; solid state NMR data; calculated and experimental electronic spectra; electrochemical data. See DOI: 10.1039/b617856a



**Fig. 1** Left: schematic representation of two peripherally octa-substituted phthalocyanines on top of each other in a columnar stack; middle: chemical structures of the phthalocyanine derivatives investigated at the theoretical level; right: the most stable conformation of dimethyl *ortho*-phthalate (view perpendicular to the ring plane) as a model for one dialkoxy-carbonyl-substituted benzene ring of the phthalocyanine macrocycle.

are out of the phthalocyanine core plane due to steric reasons. This imposes a rotation of the neighboring molecules inside the columns by an angle  $\alpha$  close to  $45^\circ$  (Fig. 1, left). This  $\alpha$  value has been shown to affect dramatically the extent of orbital splitting (*i.e.*, HOMO for holes and LUMO for electrons) and hence the charge carrier mobility.<sup>12</sup> In the specific case of a phthalocyanine core, maxima in the orbital splitting occur at  $\alpha = 0^\circ$ ,  $45^\circ$  and  $90^\circ$ .<sup>9</sup> Thus, if  $\alpha$  is close to  $45^\circ$ , as expected for octa-substituted phthalocyanines such as **B** (Fig. 1, middle), high charge carrier mobilities can be anticipated.

The electronic structures of both the unsubstituted phthalocyanine **A** and the octaalkoxy-carbonyl derivative **B** were investigated at a quantum-chemical level. In order to minimize the computational efforts, the long alkyl chains were replaced by methyl groups. This is expected to have a significant impact on the intermolecular organization but a negligible effect on the electronic structure of a single molecule. The geometry was optimized at the density functional theory (DFT) level with the B3LYP functional, using the 6-31G\* basis set within the Gaussian03 package.<sup>13</sup> In order to find the energetically favorable conformation of the COOMe groups, the potential hypersurface of dimethyl phthalate was scanned, leading to a structure where both COOMe groups are oriented in the same direction with respect to the ring plane (Fig. 1, right). This absolute minimum (*syn* conformation) is more stable by  $3.3 \text{ kJ mol}^{-1}$  than the first local minimum (*anti* conformation). We therefore used the *syn* conformation obtained for dimethyl phthalate to define a starting structure for phthalocyanine **B**, which results in dihedral angles of  $47^\circ$  and  $25^\circ$  against the ring plane. We emphasize that the exact value of the dihedral angle might somewhat vary when replacing the methyl group by a longer alkyl chain. However, the same orientation of the OR groups with respect to the ring plane is not likely to be affected.

On the basis of the DFT geometries, the electronic structures of phthalocyanines **A** and **B** were calculated at a semi-empirical Hartree-Fock level with the ZINDO/S method (Intermediate Neglect of Differential Overlap method, as parameterized by Zerner and co-workers),<sup>14</sup> coupled to a Single Configuration Interaction (CI) scheme including all  $\pi$ - $\pi^*$  single excitations. The energies of the frontier orbitals are given in Table 1. The introduction of the COOMe groups leads to a stabilization of the frontier orbitals (0.67 eV for the

HOMO and 0.74 eV for the LUMO) and overall to a slight decrease in the HOMO-LUMO energy gap.

The energies of the lowest optical transitions are given in Table 1. Note that, although the theoretical method systematically underestimates the experimental transitions of **A** by around 0.2 eV,<sup>15</sup> the relative energies and oscillator strengths of the bands are well reproduced by the calculations. The changes in the electronic structure upon substitution of H by COOMe lead to a slight bathochromic shift of the lowest  $S_1$  and  $S_2$  electronic transitions. In **A**, the  $S_1$  and  $S_2$  transitions are mainly described by the HOMO  $\rightarrow$  LUMO + 1 and HOMO  $\rightarrow$  LUMO excitations, respectively, where the small energy separation  $\Delta E(S_1, S_2)$  reflects the quasi-degeneracy of the LUMO and LUMO + 1 levels. In **B** the substituents induce a mixing of the unoccupied frontier orbitals and, thus, different CI descriptions of the transitions. In general, the low-energy part of the optical spectrum is only weakly affected by the COOR substitution (see ESI† for the calculated absorption spectra of **A** and **B**).

From all the above theoretical considerations, it can be concluded that the introduction of eight ester functions adequately increases the electron affinity of the phthalocyanine core whereas its light absorption is only weakly affected. This finding motivated us to develop a short and efficient synthesis of these promising octaalkoxy-carbonyl phthalocyanines to investigate their physical properties in greater detail.

**Table 1** Calculated energies of the frontier orbitals and energies of the lowest optical transitions together with the corresponding oscillator strengths ( $f$ ) for **A** and **B**

Value	<b>A</b> (X = H)	<b>B</b> (X = COOMe)	$\Delta E/\text{eV}^a$
LUMO + 1	-1.60 eV	-2.33 eV	-0.73
LUMO	-1.61 eV	-2.35 eV	-0.74
HOMO	-5.53 eV	-6.20 eV	-0.67
HOMO-1	-8.10 eV	-8.73 eV	-0.63
$\Delta(\text{HOMO-LUMO})$	3.92 eV	3.85 eV	-0.07
$S_1$	1.60 eV ( $f = 0.67$ )	1.57 eV ( $f = 0.80$ )	-0.03
$S_2$	1.74 eV ( $f = 0.80$ )	1.71 eV ( $f = 0.89$ )	-0.03
$S_5^b$	3.37 eV ( $f = 0.05$ )	3.19 eV ( $f = 0.19$ )	-0.18
$S_6$	3.41 eV ( $f = 0.67$ )	3.36 eV ( $f = 0.77$ )	-0.05

<sup>a</sup> Difference of the corresponding values between **A** and **B**. <sup>b</sup>  $S_3$  and  $S_4$  are symmetry forbidden transitions ( $f = 0$ ).

## Synthesis

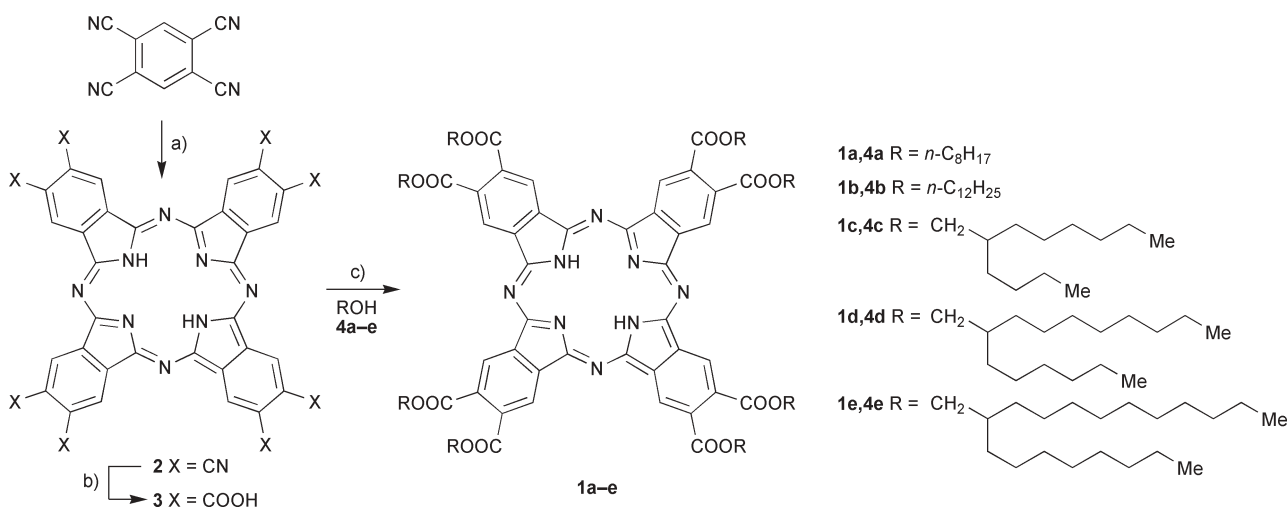
The key intermediate in the synthesis of the octaesters **1a–e** is the octanitrile **2**. It was prepared by the base-catalyzed tetramerization of 1,2,4,5-tetracyanobenzene and then hydrolyzed to the corresponding octacarboxylic acid **3** following the earlier described methods (Scheme 1).<sup>16,17</sup> Notably, no mass spectrometry data of **2** and **3** have been reported to date. However, such a characterization is highly desirable since the base-catalyzed condensation of 1,2,4,5-tetracyanobenzene may also produce oligomeric phthalocyanines due to a possible participation of the peripheral CN groups of **2** in further base-catalyzed condensations.<sup>18</sup> Octanitrile **2** does not give satisfactory mass spectra with various ionization methods, including electrospray ionization and matrix-assisted laser desorption/ionization (MALDI). However, field desorption (FD-MS) in the presence of CuCl<sub>2</sub> provided only the peak corresponding to the Cu derivative of the monomeric phthalocyanine **2** and no signals for high molecular mass oligophthalocyanines. Octaacid **3** gives the signal of the parent molecular ion together with some fragment signals in the MALDI spectra. No evidence for the presence of higher molecular mass species was found. NMR characterization of **2** and **3** is difficult due to their poor solubility and/or strong aggregation in solution that results in an extreme broadening of the signals. We have, therefore, characterized these two intermediates by magic angle spinning (MAS) solid-state NMR (see ESI†).

A derivative of phthalocyanatoiron(III) bearing eight decyloxycarbonyl groups in the *peripheral* positions was prepared earlier from the corresponding octaacid *via* conversion into acyl chloride followed by reaction with *n*-decyl alcohol in pyridine.<sup>19</sup> The synthesis of metal-free octaesters **1a,b** by alkylation of octaacid **3** with *n*-alkyl halides in the presence of a non-nucleophilic base (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) has also been reported earlier.<sup>17</sup> However, low yields and tedious purification render this method rather impractical. Therefore, we have developed a new, straightforward and convenient synthesis of octa-substituted phthalocyanines **1a–e** with linear or branched alkyl

substituents in up to 78% yield by the esterification of the acid **3** with alcohols **4a–e** upon azeotropic removal of water. It should be noted that the esterification proceeds relatively slowly because of the extremely low solubility of **3** in the reaction medium. Problems with esterification of badly soluble aromatic polyacids requiring non-trivial esterification procedures have been reported earlier.<sup>20</sup> The branching of alkyl chains does not affect substantially the yield of the reaction, as expected.

Octaesters **1a–e** were isolated by simple flash chromatography on SiO<sub>2</sub>. However, in some cases it was difficult to separate the product from the excess of the starting alcohols. In order to obtain compounds of high purity, as required for the characterization of the phase behavior, we used three methods based on the very low solubility of phthalocyanines **1a–e** in methanol. Traces of alcohol were removed either by the repetitive liquid–liquid extraction in a two-phase hexane–methanol system or by precipitation of phthalocyanines from the hexane solution by slow addition of methanol. However, the following chromatography procedure turns out to be the most convenient and general method of purification: the crude product was applied on the SiO<sub>2</sub> column and the excess of the starting alcohol together with other eventual impurities was eluted with methanol. Due to their insolubility in methanol, the target phthalocyanine derivatives remained adsorbed on SiO<sub>2</sub> and were then eluted with an appropriate solvent (detailed purification procedures for individual compounds are described in the ESI†).

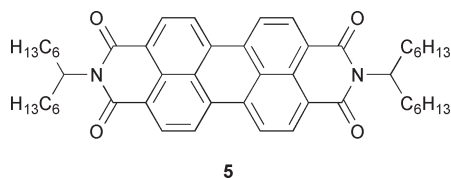
All phthalocyanines **1a–e** are well soluble in common organic solvents and were characterized by <sup>1</sup>H and <sup>13</sup>C NMR and by MALDI MS. The UV-visible absorption spectra of **1a–e** in solution are nearly identical and show a small bathochromic shift of the two long-wavelength absorptions (S<sub>1</sub>, S<sub>2</sub>) forming the so-called Q-band compared to the unsubstituted phthalocyanine **A**.<sup>21</sup> The shifts amount to 0.015 and 0.012 eV for S<sub>1</sub> and S<sub>2</sub>, respectively. Quantum-chemical calculations predict a similar small bathochromic shift of 0.03 eV, see Table 1.



**Scheme 1** Synthesis of **1a–e**. Reagents and conditions: a) *n*-PrOLi, *n*-PrOH, reflux; b) KOH, H<sub>2</sub>O, triethylene glycol, 190 °C; c) TsOH, toluene, reflux. Ts = tosyl, 4-(methyl)phenylsulfonyl.

## Electrochemistry

Electrochemical studies on the metal-free phthalocyanines **1b** and **1c** were performed by cyclic voltammetry (CV), using a platinum wire as working and counter electrode and a secondary Ag/AgCl electrode. A range of concentrations and scan rates (from 10 to 500 mV s<sup>-1</sup>) was investigated. Both **1b** and **1c** showed poorly resolved voltammograms in dichloromethane, with peak currents approaching zero. However, when cyclic voltammograms were recorded in THF instead of CH<sub>2</sub>Cl<sub>2</sub>, four resolved quasi-reversible reduction waves were observed within the available potential range, centered at  $E_{1/2} = -1.08, -1.48, -2.27$  and  $-2.61$  V for **1b** and  $E_{1/2} = -1.07, -1.48, -2.27$  and  $-2.62$  V for **1c** (vs. Fc/Fc<sup>+</sup>, representative CV curves are given in the ESI†). No remarkable difference in the formal reduction potentials was observed between **1b** and **1c**. These one-electron reductions can be assigned to the characteristic ring-based electrochemistry of metal-free phthalocyanines.<sup>22,23</sup> The relatively good electron acceptor ability of these materials is evidenced by the position of the reduction waves, which appear at comparable values to the perylene tetracarboxydiimides (PDI). Thus, *N,N'*-dialkyl PDI **5** gave reduction waves at  $E_{1/2} = -1.07$  and  $-1.45$  V in identical experimental conditions. PDI derivatives are often used as electron acceptors in molecular and supramolecular architectures.<sup>24</sup> Recently, an electron mobility of 1.3 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in the columnar mesophase of liquid crystalline PDI derivatives in the ambient atmosphere was reported.<sup>25</sup> These results suggest the electron withdrawing alkyl ester functions of **1a–e** sufficiently modify the electron affinity of the phthalocyanine core to obtain air-stable n-type semiconductors.<sup>26</sup>



None of the recorded reduction waves of **1b** and **1c** exhibits ideal reversible behavior. Electrochemical reversibility for one-electron processes at 25 °C is characterized by peak potential differences of 59 mV and is independent of scan rate.<sup>27</sup> The relatively high difference between the peak anodic and cathodic potentials ( $\Delta E_p$ , ca. 0.25 V) suggests that the electron transfer rate between the electrode and the electroactive core is greatly hampered by the peripheral substituents. Similar electrochemical behavior has been reported for phthalocyanines bearing long-chain peripheral substituents.<sup>23</sup> Interestingly,  $\Delta E_p$  for metal-free octaalkyl phthalocyanines progressively grows as the side chain length increases. One may assume that flexible side chains wrap around the phthalocyanine core to form a globule that partially isolates it from the electrode.<sup>23</sup> Another possible reason can be related to the pronounced aggregation in THF, as evidenced by the <sup>1</sup>H NMR studies (see below).

In spite of the rich electrochemistry of the cathodic part of the voltammograms, no oxidation processes were observed. This may be due to the presence of the eight

electron-withdrawing peripheral alkoxy-carbonyl substituents that strongly shift the oxidation potential towards more positive values, as reported recently for palladium phthalocyanine bearing alkylsulfonyl substituents.<sup>28</sup> Thus, the oxidation processes of octaalkoxy-carbonyl phthalocyanines may be expected beyond the electrochemical window of THF.

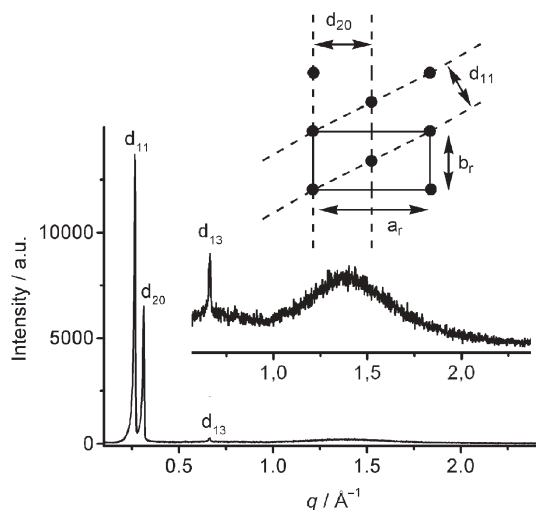
## Characterization of mesophases

Octa-substituted phthalocyanines **1a,b** with linear *n*-alkyl substituents reportedly form columnar liquid crystalline phases in an exceptionally wide temperature range (above -60 °C for **1a** and above 12 °C for **1b**, no isotropization until 300 °C).<sup>17</sup> Although we confirmed the wide mesophase range for **1a,b** and did not observe clearing points below 300 °C, the phase behavior was considerably different from that earlier described. Thus, **1a** showed a clear transition between the crystalline (Cr) and the columnar hexagonal (Col<sub>h</sub>) phases at 85 °C upon heating [enthalpy 90.3 kJ mol<sup>-1</sup>], and the Cr-Col<sub>h</sub> transition for **1b** takes place at 62 °C [132.5 kJ mol<sup>-1</sup>]. The large hysteresis with transitions observed on cooling (onset of the DSC cooling curve 2 °C [91.5 kJ mol<sup>-1</sup>] for **1a**, 30 °C for **1b** [143.8 kJ mol<sup>-1</sup>]) is likely due to high viscosity of the liquid crystalline mesophase that prevents crystallization. The incorrect transition temperatures of **1a,b** reported by Dulog and Gittinger<sup>17</sup> might be due to the insufficient purity of compounds.

Thus, **1a,b** are not liquid crystalline at room temperature and therefore not practical for the fabrication of realistic devices. In addition, the clearing point is not observable until 300 °C, and therefore, these materials are unsuitable for processing of thin films by thermal annealing: the upper temperature limit for fabrication of devices on flexible plastic substrates is considered to be 200 °C.<sup>29</sup>

It has been well documented that branched peripheral substituents promote the formation of mesophases and decrease both the temperature of the transition between crystalline and LC phases and the isotropization temperature of discotic molecules compared to analogs with linear substituents.<sup>30,31</sup> This is largely due to the increased steric hindrance that reduces the  $\pi$ - $\pi$  stacking of the flat aromatic cores. Indeed, **1c** bearing the more sterically demanding 2-butyloctyl peripheral chains is liquid crystalline at ambient conditions and its isotropization temperature is dramatically reduced compared to the straight-chain isomer **1b** (DSC data: transition onset 150 °C [8.2 kJ mol<sup>-1</sup>] on heating, 149 °C [8.3 kJ mol<sup>-1</sup>] on cooling; no other transition was observed). Further elongation of the branched substituents in **1d** and **1e** produces materials that remain isotropic even at room temperature.

The dendritic textures revealed by polarized optical microscopy (POM, see ESI† for a representative example) upon heating **1c** between two glass slides followed by slow cooling below the clearing point (150 °C) suggest the columnar nature of this liquid crystalline phase. This phase was studied by powder X-ray diffraction as a function of temperature. In agreement with the DSC data, only one columnar mesophase is observed between room temperature and the clearing point. It possesses a 2D rectangular centered lattice, as evidenced by two sharp fundamental peaks in the diffraction pattern (Fig. 2).



**Fig. 2** X-Ray powder diffraction pattern of **1c** at 25 °C and a schematic representation of the two-dimensional lattice of **1c**; black dots represent the centers of gravity of discotic molecules; the lattice cell with parameters  $a_r$  and  $b_r$  ( $\gamma$  angle is 90°) is shown with solid lines.

The less intense of these two peaks corresponds to the fundamental reflection (20) while the more intense peak is indexed as the (11) reflection (the (11) scattered intensity is twice as large as the (20) intensity due to the reflection multiplicity). In addition, a unique Bragg reflection at  $0.65 \text{ \AA}^{-1}$  indexed as (13) is observed. The broad diffuse halo at a higher  $q$  range ( $q > 1.0 \text{ \AA}^{-1}$ ) originates from liquid-like disordered aliphatic chains. No reflection peak at  $ca. 1.8 \text{ \AA}^{-1}$  characteristic of the  $\pi$ - $\pi$  stacking is observed, thus indicating a poor order along the columnar axis.<sup>9</sup>

There are two possible planar symmetry groups for the observed rectangular columnar ( $\text{Col}_r$ ) phase, namely  $p2gg$  and  $c2mm$  (see ESI†).<sup>32</sup> They can be distinguished on the basis of higher order reflections. Indeed, for  $p2gg$  symmetry the reflections  $h0$  and  $0k$  should satisfy the conditions  $h = 2n$  and  $k = 2n$ , respectively. In addition, in  $c2mm$  symmetry group reflections with  $h + k = 2n + 1$  are forbidden. Given that the (31) reflection is observed and the (21) reflection is absent,  $c2mm$  symmetry can be assigned to the  $\text{Col}_r$  phase under discussion. At the same time, this assignment should be treated with caution, since the observed (31) reflection is allowed in

both plane groups, and no other Bragg reflections are observed due to relatively low order of the mesophase.<sup>33</sup>

Variable temperature X-ray measurements revealed no significant structural variation and only a slight lattice area compression (see ESI†). This negative thermal expansion effect was recently reported for the columnar phases of polycatenar mesogens.<sup>33</sup>

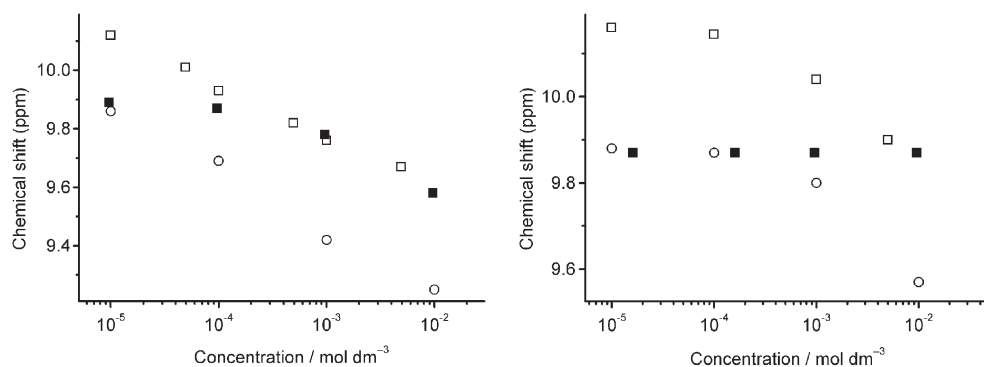
### Self-aggregation in solution

As mentioned in the Introduction, self-organization of discotic molecules in solution is important for their processing and hence for the performance of devices based on such materials. Molecules with pronounced tendency to aggregate have been shown to be the best candidates to yield ordered thin films by solution zone-processing.<sup>3</sup>

Phthalocyanines and other disk-like molecules are known to aggregate in solution due to efficient  $\pi$ - $\pi$  cofacial interactions. The concentration dependence of the aromatic resonances in  $^1\text{H}$  NMR spectra is considered as a “signature” of aggregation and can be used as a sensitive probe for this phenomenon. The ring current of the aromatic core induces a shift of the resonances of the neighboring molecules. Since the interacting disk-like molecules are typically in an offset face-to-face arrangement, self-aggregation leads to an upfield shift of the aromatic resonances.<sup>34</sup>

We have investigated the aggregation of **1b** and **1c** by  $^1\text{H}$  NMR in various solvents in the concentration range between  $10^{-2}$  and  $10^{-5}$  M (Fig. 3). Due to the pseudo  $D_{4h}$  symmetry of octa-substituted phthalocyanine molecules (the exchange of protons between the inner nitrogen atoms is fast on the NMR time scale),  $^1\text{H}$  NMR spectra display only one singlet of the aromatic proton that can easily be monitored. As expected, **1b** bearing linear alkyl chains strongly aggregates in all studied solvents, as evidenced by the pronounced concentration dependence of the chemical shifts of the aromatic protons. In contrast, phthalocyanine **1c** with branched chains shows no observable aggregation in  $\text{CDCl}_3$ . This is attributed to the steric hindrance imposed by the bulkier substituents that prevents efficient  $\pi$ - $\pi$  stacking.

A similar influence of the substituent nature on aggregation was observed in other solvents. While the aromatic resonance of **1c** approaches a plateau at  $10^{-5}$  M in both  $\text{THF-d}_8$  and  $\text{C}_6\text{D}_6$ , thus suggesting the presence of only monomeric species



**Fig. 3** Concentration-dependent  $^1\text{H}$  chemical shifts of aromatic protons in **1b** (left) and **1c** (right) recorded at 25 °C in  $\text{CDCl}_3$  (■),  $\text{C}_6\text{D}_6$  (□) and  $\text{THF-d}_8$  (○).

in solution, **1b** appears to be much strongly aggregated at this concentration. Further elongation of the branched substituents (**1d** and **1e** vs. **1c**) has only insignificant influence on the self-aggregation in C<sub>6</sub>D<sub>6</sub> (see ESI†). Another typical feature of the <sup>1</sup>H NMR spectra of **1b** in THF-d<sub>8</sub> and C<sub>6</sub>D<sub>6</sub> is a considerable line broadening due to the strong aggregation.

It should be noted that the self-aggregation of both **1b** and **1c** is strongly dependent on the nature of the solvent. While the aromatic resonances of the two phthalocyanines as a function of concentration follow the same general trend in THF-d<sub>8</sub> and C<sub>6</sub>D<sub>6</sub>, the behavior in CDCl<sub>3</sub> is dramatically different. CDCl<sub>3</sub> reduces self-association in solution for both **1b** and **1c** while C<sub>6</sub>D<sub>6</sub> and THF-d<sub>8</sub> favor aggregation. It thus appears that the interactions between the molecules of solvent and the solute are much more efficient in CDCl<sub>3</sub> than in the other two solvents. The similar behavior of the studied phthalocyanines in THF-d<sub>8</sub> and C<sub>6</sub>D<sub>6</sub> is rather unexpected since aromatic solvents are assumed to interact with the discotic molecules by π–π interactions and hence to efficiently suppress the self-aggregation. Dramatically enhanced association in benzene was reported recently for hexaalkyl hexabenzocoronenes; but also here the experimental finding remained unexplained.<sup>3</sup> It has recently been also found that the nature of the solvent dramatically influences the formation and stability of one-dimensional stacks of oligo(*para*-phenylenevinylene) derivatives.<sup>35</sup>

## Conclusions

In summary, we have reported a series of octaalkoxycarbonyl phthalocyanines that could find application in organic electronic devices on the basis of their interesting properties. Quantum-chemical calculations predict a strong decrease in the energy of the HOMO and LUMO levels, as required to promote electron (n-type) transport at ambient conditions. This conclusion is further supported by the electrochemical studies, which show good electron acceptor ability of octaalkoxycarbonyl phthalocyanines. Short synthesis and simple purification allow the preparation of **1a–e** on a multi-gram scale, which is a prerequisite for a material to find practical applications. The variation of the peripheral substituents represents an efficient way to adjust the thermotropic properties of these novel discotic mesogens. In particular, a liquid crystalline columnar mesophase between the ambient temperature and the reasonably low clearing point (150 °C) was observed for **1c**.

Self-aggregation of octaalkoxycarbonyl phthalocyanines in solution can be efficiently tuned by either structural variations of the peripheral substituents or by changing the nature of the solvent. Phthalocyanines bearing the less sterically demanding linear alkyl chains combine high solubility in organic solvents with a pronounced tendency towards self-aggregation in solution and appear to be good candidates for zone-casting processing. It thus appears that contradictory requirements should be fulfilled in order to obtain a material suitable for different processing methods. The inter-disk interactions should be sufficiently strong to ensure aggregation in solution and, at the same time, adequately weak to provide a reasonably low isotropization temperature in the bulk. However,

upon appropriate choice of the solvent, even the phthalocyanines with the more sterically demanding branched substituents aggregate in solution.

All important prerequisites for the fabrication of n-type semiconductor devices by the combination of solution processing and thermal annealing methods are thus fulfilled for the phthalocyanine **1c**. We are currently working on the fabrication of aligned films of liquid crystalline octaalkoxycarbonyl phthalocyanines. Further objectives include studies of electron transport in the columnar mesophases and the fabrication of devices incorporating these materials.

## Experimental

### Materials and methods

All chemicals were purchased from Aldrich or Acros and used without further purification unless stated otherwise. All reactions were carried out under dry Ar. <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra were recorded on a Bruker Avance 300 spectrometer; chemical shifts (δ) are given in ppm relative to Me<sub>4</sub>Si (internal standard); coupling constants (*J*) are given in Hz. Details of MAS NMR measurements are given in the ESI.† MALDI-TOF mass spectra were measured on a Bruker Reflex II, with dithranol as a matrix; FD mass spectra were measured on a VG-Instruments ZAB 2-SE-FDP; *m/z* with the lowest isotopic mass are reported. Phase transition temperatures were determined by differential scanning calorimetry (Mettler Toledo DSC 821) from the onsets of the second heating and the second cooling curves. Optical textures were observed with a polarizing microscope (Nikon Eclipse 80i). UV-Vis spectra were recorded on a Hewlett-Packard 8453 spectrophotometer. Phthalocyanines **2** and **3** were synthesized according to published procedures.<sup>16,17</sup>

Powder X-ray diffraction measurements were performed on a Bruker D8 Advance diffractometer using Cu-Kα radiation (λ = 1.5418 Å). All samples were prepared on thin pre-cleaned aluminium plates. Diffraction patterns were collected in the scattered angular range between 1.5° and 60° with the angular resolution 0.02° per step and a typical counting time of 10 s per step, using the Bragg–Brentano geometry (θ/2θ set-up). X-Ray spectra are given as the scattering intensity versus the wave-vector transfer  $q = 4\pi \sin(\theta)\lambda^{-1}$  [Å<sup>-1</sup>]. The sample temperature was controlled within a 0.1 °C accuracy. To ensure reproducibility of results, several heating and cooling cycles were performed using the same sample.

Cyclic voltammetry experiments were performed with a computer controlled EG&G PAR 273 potentiostat in a three-electrode single-compartment cell (2 ml) under inert atmosphere. The platinum working electrode consisted of a platinum wire sealed in a soft glass tube with a surface of *A* = 0.785 mm<sup>2</sup>, which was polished down to 0.5 μm with Buehler polishing paste prior to use in order to obtain reproducible surfaces. The counter electrode consisted of a platinum wire and the reference electrode was a Ag/AgCl secondary electrode. All potentials were internally referenced to the ferrocene–ferrocenium (Fc/Fc<sup>+</sup>) couple. All solutions were prepared in freshly distilled anhydrous and deaerated CH<sub>2</sub>Cl<sub>2</sub> or THF containing 0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>] (TBAPF<sub>6</sub>,

Fluka), which was recrystallized twice from ethanol and dried in vacuum prior to use.

### Synthesis of octaesters 1a–e

**Representative procedure: 2,3,9,10,16,17,23,24-octakis(2-butyltolyl-1-oxy-carbonyl)-29H,31H-phthalocyanine, mixture of diastereoisomers (1c).** A 100 cm<sup>3</sup> round-bottom flask was equipped with a pressure-equalizing addition funnel charged with *ca.* 20 g of 4 Å molecular sieves. A reflux condenser was placed on the top of the funnel so that the system operates in a fashion of a Soxhlet extractor. The flask was charged with **3** (433 mg, 0.5 mmol), **4c** (2.25 cm<sup>3</sup>, 10 mmol), TsOH (200 mg), and toluene (60 cm<sup>3</sup>) and heated at vigorous reflux for 48 h. The reaction mixture was filtered through a plug of Celite and concentrated *in vacuo*. The residue was purified by flash chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>–AcOEt 50 : 1) to give a crude product, containing a small amount of **4c**. The crude product was partitioned between hexane (50 cm<sup>3</sup>) and methanol (50 cm<sup>3</sup>), the upper green layer was separated, methanol (50 cm<sup>3</sup>) was added and the extraction was repeated 3 more times. The upper hexane layer was concentrated *in vacuo* to give **1c** (870 mg, 78%) as a dark-green waxy solid (Found: C, 73.7%; H, 9.5%; N, 5.1%. C<sub>136</sub>H<sub>210</sub>N<sub>8</sub>O<sub>16</sub> requires C, 73.8%; H, 9.6%; N, 5.1%); λ<sub>max</sub> (CHCl<sub>3</sub>)/nm 350 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 94 100), 649 (53 200), 668 (173 000), 705 (190 000); δ<sub>H</sub> (300 MHz, 0.01 mol dm<sup>-3</sup> in CDCl<sub>3</sub>, Me<sub>4</sub>Si, 25 °C) 9.87 (8 H, s, arom. H), 4.53 (16 H, d, *J* 6.0, CH<sub>2</sub>O), 2.02 (8 H, m, CHCH<sub>2</sub>O), 1.20–1.70 (128 H, m, CH<sub>2</sub>), 1.00 (24 H, t, *J* 7.0, Me), 0.87 (24 H, t, *J* 6.9, Me), –0.17 (2 H, br s, NH); δ<sub>C</sub> (75 MHz, 0.01 mol dm<sup>-3</sup> in CDCl<sub>3</sub>, Me<sub>4</sub>Si, 25 °C) 167.8, 137.9, 134.7, 124.6, 69.6, 37.5, 31.9, 31.4, 31.1, 29.7, 29.0, 26.8, 23.1, 22.7, 14.2, 14.1; *m/z* (MALDI) 2211.6 (M<sup>+</sup>).

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