

Ester-functionalized phthalonitriles and zinc phthalocyanines via palladium-catalyzed cyanation of 4,5-dichlorophthalates

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Abstract

Dicyanophthalates **3** were synthesized via Pd-catalyzed two-fold cyanation of the corresponding 4,5-dichlorophthalates with $\text{Zn}(\text{CN})_2$. Appropriate modification of reaction conditions allowed one-pot synthesis of the corresponding zinc phthalocyanines **7** bearing eight peripheral alkyl ester groups. Powder X-ray diffraction study of a mesogenic zinc phthalocyanine bearing branched alkyl substituents revealed a rare case of a transition between two columnar rectangular liquid crystalline mesophases with different symmetry.

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Keywords: Phthalocyanines; Phthalonitriles; Palladium; Cyanation

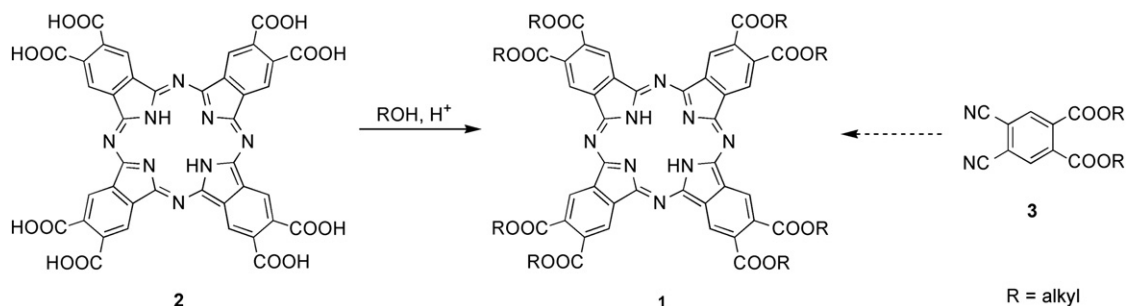
1. Introduction

Phthalocyanines have found a number of important industrial applications as dyes and pigments due to their bright blue or green colors combined with extraordinary thermal and photochemical stability.¹ 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.^{2,3} Mesogenic phthalocyanines bearing flexible peripheral substituents have been widely studied for applications in electronic devices and have demonstrated very efficient charge transport.⁴ Combination of charge transport capacity with very strong absorption of visible light makes them promising candidates for photovoltaic applications. Our research is focused around phthalocyanines for applications in organic electronic devices, including photovoltaic cells. In particular, we are interested in liquid crystalline, solution-processable phthalocyanines bearing electron-withdrawing groups as acceptor components for bulk heterojunction photovoltaic cells.

Recently, we have reported^{5,6} the synthesis of octaester derivatives of metal-free phthalocyanines (**1**, Scheme 1) via the eight-fold esterification of octaacid **2**. Major disadvantages of this method are rather long reaction times due to very limited solubility of the octaacid **2** in virtually all organic solvents and the necessity to perform conversion of eight functional groups in one molecule. In addition, when the resulting octaester was also only poorly soluble in the reaction medium (what was the case for shorter alkyl substituents or for partially fluorinated alkyls), the yields of the esterification dropped dramatically. Finally, the two-step synthesis of the octaacid **2** from 1,2,4,5-tetracyanobenzene is rather time-consuming.⁷ Therefore, we became interested in designing an alternative synthetic pathway to phthalocyanines such as **1**, starting from well-soluble precursors. Since phthalocyanines are commonly prepared by the tetramerization of suitably functionalized *ortho*-phthalonitriles, dialkyl dicyanophthalates **3** appear as most obvious synthetic intermediates for this approach. Here, we report on the efficient synthesis of ester-functionalized phthalonitriles **3** via Pd-catalyzed cyanation as well as on related studies on the synthesis and characterization of metal-free phthalocyanines and their zinc analogs.

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Scheme 1. Two possible synthetic approaches to octa(alkoxycarbonyl)phthalocyanines.

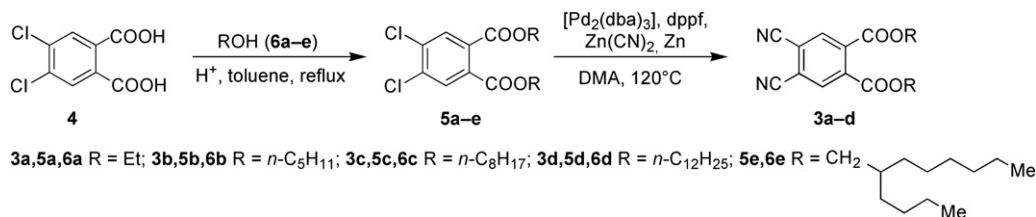
2. Results and discussion

Neither the dicyanophthalates **3** nor the parent 4,5-dicyanophthalic acid is described in the chemical literature. We have therefore developed a two-step synthesis of a series of phthalonitriles **3a–d** starting from the commercially available 4,5-dichlorophthalic acid **4** (Scheme 2). First, the corresponding 4,5-dichlorophthalates **5a–d** with linear alkyl radicals of various lengths were prepared in 72–90% yield by a standard acid-catalyzed esterification of **4** with alcohols **6a–d** upon azeotropic removal of water with toluene. Diethyl ester **5a**⁸ was purified by crystallization, while longer-chain homologs **5b–d** required chromatography on a short column to remove the excess of alcohol.

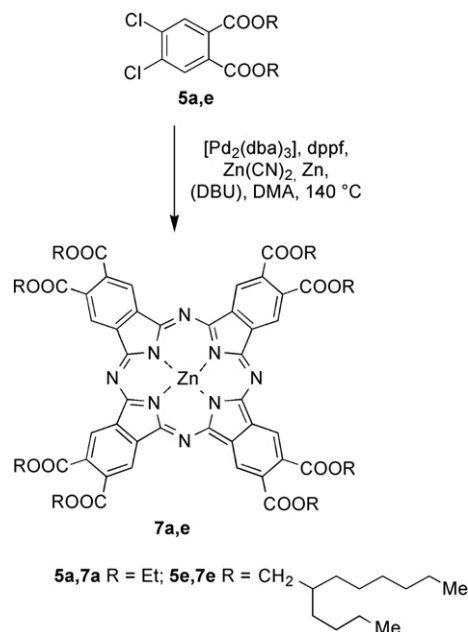
The reaction of metal cyanides with aryl halides is a well-known general methodology for the synthesis of aromatic nitriles.⁹ Classically known as the Rosenmund–von Braun reaction, it typically requires rather harsh conditions and allows substitution of bromine or iodine, but not of chlorine. However, this useful transformation was greatly improved in recent years by application of transition metal complexes as catalysts. It allows, upon appropriate choice of a catalyst, to carry out halogen–CN displacement in rather deactivated substrates.¹⁰ For the conversion of dichlorophthalates **5a–d** to the corresponding dinitriles **3a–d**, we have adapted the Pd-catalyzed cyanation protocol that proved efficient in various chlorine–CN substitutions.¹¹ Air-stable [Pd₂(dba)₃] and an activating ligand, dppe (1,1'-bis(diphenylphosphino)ferrocene), were used as an efficient catalytic system. The combination of Zn(CN)₂ as a cyanide source with catalytic amounts of Zn allows to avoid the CN[−]-induced deactivation of the catalyst. Starting from dichlorophthalates **5a–d**, the corresponding ester-functionalized phthalonitriles **3a–d** were obtained in 72–83% yield after 2 h in *N,N*-dimethylacetamide (DMA) at 120 °C.

With the necessary key intermediates in hands, we tried next the condensation of phthalonitriles **3a–d** to the corresponding octaester derivatives of phthalocyanines **1**. Common protocols for the synthesis of phthalocyanines from phthalonitriles involve lithium alcoholates and are clearly incompatible with ester functions. However, milder procedures using a non-nucleophilic base (DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene)¹² or cerium-promoted condensation of phthalonitriles¹³ were unsuccessful either. Although some phthalocyanines were obviously produced, as can be judged by the intense green color of reaction mixtures, no individual compounds were isolated. Finally, a recently reported mild procedure using propanone or butanone oximes¹⁴ as weak bases and at the same time, as reducing agents (condensation of four molecules of a phthalonitrile to give a phthalocyanine molecule formally requires donation of two electrons and two protons) resulted largely in the recovery of the starting materials and produced only traces of desired phthalocyanines. Thus, **3c** gave 5% of the corresponding metal-free phthalocyanine **1** (R = *n*-C₈H₁₇). Spectral data of the latter were identical to those of a material prepared by the esterification of the octaacid **2** with *n*-octanol.⁵ Since the original esterification method gave much higher yields of the corresponding phthalocyanines (60–64% from the octaacid **2**), we decided to discontinue the attempts to optimize the condensation of phthalonitriles **3**.

However, in the above described Pd-catalyzed cyanation of dichlorophthalates **5a–d**, we paid attention to the greenish color of the reaction mixture. This clearly indicated an *in situ* formation of trace amounts of phthalocyanines from the initially formed phthalonitriles. At elevated temperatures and longer reaction times, this pathway became a dominating one. Thus, only a minute amount of dinitrile **3a** was isolated after 16 h from the reaction between diethyl dichlorophthalate **5a** and Zn(CN)₂ in DMA at 140 °C. Instead, column chromatography afforded 13% of the rather poorly soluble zinc

Scheme 2. Synthesis of diesters **5a–e** and dinitriles **3a–d**; dba=dibenzylideneacetone, dppe=1,1'-bis(diphenylphosphino)ferrocene, DMA=*N,N*-dimethylacetamide.

phthalocyanine **7a** (Scheme 3), structure of which was established by ^1H NMR, MALDIMS, and UV–vis spectroscopy.¹⁵ We thus observed an interesting and to the best of our knowledge previously unknown one-pot transformation of an *ortho*-dichlorobenzene derivative to a Zn-phthalocyanine. Also, this is only the second reported example of a metallated phthalocyanine derivative bearing peripheral ester groups.¹⁶



Scheme 3. One-pot conversion of dichlorophthalates **5** into zinc phthalocyanines **7**; dba=dibenzylideneacetone, dppf=1,1'-bis(diphenylphosphino)ferrocene, DMA=*N,N*-dimethylacetamide, DBU=1,8-diazabicyclo[5.4.0]undec-7-ene.

We speculated that the rather low yield of the ester-functionalized zinc phthalocyanine **7a** might be due to its poor solubility in organic solvents. We have therefore attempted to apply this method to the synthesis of zinc phthalocyanine **7e** bearing eight branched alkyl substituents. This target molecule was chosen since branched alkyl substituents are well known to reduce intermolecular cofacial interactions between flat phthalocyanine cores both in solution and in the solid state much more efficiently compared to the linear homologs. This results in greatly improved solubility in common organic solvents and in the formation of liquid crystalline (LC) columnar mesophases over broad temperature range. Both features are highly relevant for materials intended for the use in organic electronic devices.¹⁷

Thus, we have synthesized bis(2-butyloctyl)-4,5-dichlorophthalate **5e** by the same esterification procedure as described above for the linear homologs **5a–d**. However, starting from **5e**, only 6% of Zn-phthalocyanine **7e** was isolated after 16 h in DMA at 140 °C. We reasoned that addition of a non-nucleophilic base such as DBU may increase the yield of **7e**. However, only marginal improvement (10% of **5e** from **7e**) was achieved and the yield thus remained rather low. We noticed that a considerable amount of (presumably) phthalocyanine derivatives remained non-isolable during workup and purification, as was judged by the very intense green color of the aqueous phases after extraction and of the chromatography

sorbent. We therefore assume that cleavage of ester groups took place to give highly polar products with free carboxyl groups.

The isolated ester-functionalized zinc phthalocyanine **7e** was characterized by various physicochemical methods. MALDIMS measurements confirmed the absence of the metal-free phthalocyanine **1e** and of the corresponding palladium phthalocyanine (formation of the latter cannot a priori be excluded in the Pd-catalyzed reaction). The exact molecular mass of **7e** is in excellent agreement with the calculated value. The UV spectrum of **7e** in CH_2Cl_2 is typical for a metallated phthalocyanine and features a single intense low-frequency absorption band (termed Q-band) due to a degenerate first excited state of a D_{4h} -symmetrical molecule (cf. a split of Q-band due to the loss of degeneracy in the metal-free phthalocyanine **1e** with lower D_{2h} symmetry, Fig. 1).

^1H NMR spectrum of zinc phthalocyanine **7e** in CDCl_3 indicates strong aggregation, as evidenced by very broad signals. This is due to the propensity of the central Zn^{2+} ion for pentacoordination, which results in efficient interaction with nitrogen atoms of neighboring phthalocyanine molecules. However, when an excess of deuterated pyridine ($\text{C}_5\text{D}_5\text{N}$) is added to a solution, it acts as a competing ligand and well-resolved ^1H and ^{13}C NMR spectra are obtained due to greatly diminished aggregation (see Supplementary data).

Another property of phthalocyanines that is well known to be significantly affected by cofacial inter-disk interactions and therefore, by the nature of the central metal ion is the thermal stability of columnar LC mesophases. Indeed, according to polarized optical microscopy (POM) data, **7e** forms LC mesophases between room temperature and ca. 250 °C (clearing point determined by POM; more precise measurement of isotropization temperature by differential scanning calorimetry (DSC) was not possible because of slow decomposition of **7e** at high temperatures). Thus, the isotropization temperature of **7e** is ca. 100 °C higher than that of the corresponding metal-free analog **1e** bearing identical peripheral groups.⁵ A similar effect of the central zinc atom on the stability of

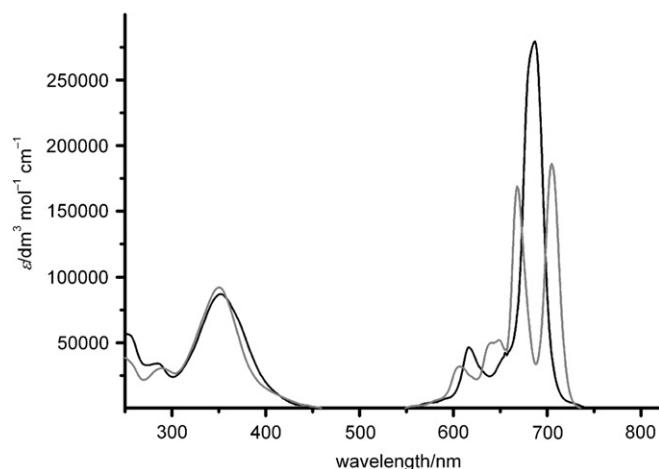


Figure 1. UV–vis absorption spectra of metal-free phthalocyanine **1e** (gray line) and zinc phthalocyanine **7e** (black line) bearing identical peripheral substituents; spectra recorded in CH_2Cl_2 .

columnar LC mesophases was reported earlier for octaalkylphthalocyanines.^{2,18}

A typical dendritic structure observed by POM after cooling of **7e** between two glass slides from isotropic melt below clearing point suggests a columnar LC phase. Upon further cooling down to room temperature no significant change in the POM texture was observed. However, DSC measurements revealed one more reversible transition at lower temperatures (heating: 44 °C [1.1 kJ mol⁻¹], cooling: 30 °C [1.0 kJ mol⁻¹]). Relatively small enthalpy suggests only a minor change in the structure of the material, that is, a transition between two different LC phases. This assumption has been confirmed by powder X-ray diffraction of **7e** at different temperatures. X-ray diagrams at 30 and 100 °C are shown in Figure 2; for the detailed evolution of the X-ray diffraction patterns as a function of temperature, see Supplementary data.

X-ray diffraction patterns of **7e** at 30 and 100 °C are very similar. They both exhibit two sharp, intense diffraction peaks together with less intense higher order peaks in the small angle region ($q < 1.2 \text{ \AA}^{-1}$), thus suggesting 2D rectangular lattices (Col_r). A broad diffuse halo at $q > 1.2 \text{ \AA}^{-1}$ originates from

liquid-like disordered aliphatic chains, characteristic for LC phases. No reflection in the q range $1.7\text{--}1.8 \text{ \AA}^{-1}$, which would correspond to the π – π stacking distance was observed, thus indicating a poor order along the columnar axis. Thus, similar to the metal-free analog **1e**, zinc phthalocyanine **7e** forms relatively disordered Col_r phases.⁵

The cell parameters of low temperature and high temperature LC mesophases (Col_{r1} and Col_{r2}, respectively) are very close to each other (see Supplementary data). However, some clear differences between the X-ray diffraction patterns of Col_{r1} and Col_{r2} were observed. Firstly, the positions of the (20) reflection are slightly different and the gradual change of this position was clearly observed on heating or cooling across the transition temperature between Col_{r1} and Col_{r2} (see Supplementary data). Secondly, a broadening of the peak in the q range $0.6\text{--}0.7 \text{ \AA}^{-1}$ upon transition from Col_{r1} to Col_{r2} is due to the appearance of the (32) reflection. Therefore, on the basis of higher order reflections two different planar symmetry groups $C2mm$ and $P2gg$ can be assigned to mesophases Col_{r1} and Col_{r2}, respectively. Indeed, for $P2gg$ symmetry the reflections $h0$ and $0k$ should satisfy the conditions $h=2n$ and $k=2n$. In addition, in $C2mm$ symmetry group reflections with $h+k=2n+1$ are forbidden. Hence, the (32) reflection observed for Col_{r2} is only possible for $P2gg$ plane group, whereas the base-centered $C2mm$ plane group has been assigned to Col_{r1}. A similar transition between two Col_r LC phases of different symmetry has been reported for some mesogenic disc-like metal–ligand complexes,¹⁹ but to the best of our knowledge, it is unprecedented for phthalocyanine derivatives.

Taking advantage of its enhanced solubility, zinc phthalocyanine **7e** was chosen for electrochemical studies, which were performed by cyclic voltammetry (CV) using a platinum wire as working and counter electrode and a reference Ag/AgCl electrode. Unlike the metal-free phthalocyanine **1e**,⁵ zinc phthalocyanine **7e** showed poorly resolved voltammograms in THF with peak currents approaching zero. However, in CH₂Cl₂ well-resolved quasi-reversible reduction

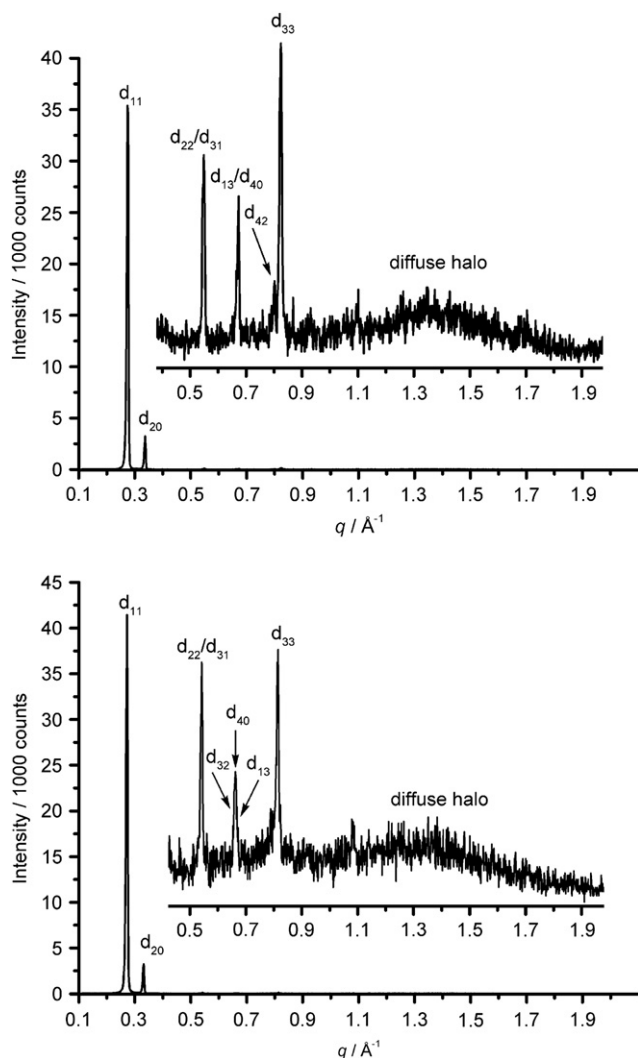


Figure 2. X-ray diffraction patterns of **7e** at 30 °C (Col_{r1}; top) and 100 °C (Col_{r2}; bottom).

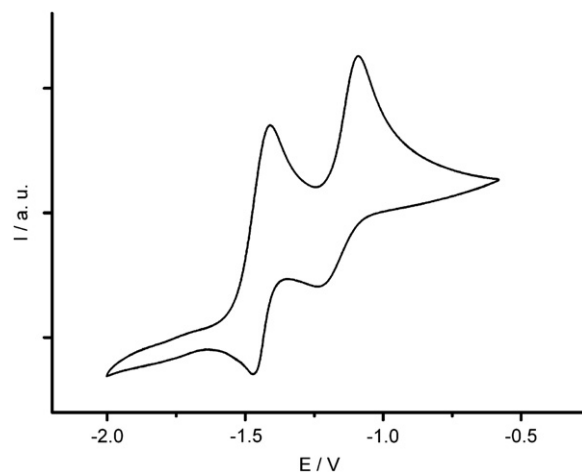


Figure 3. Cyclic voltammogram of **7e** in CH₂Cl₂ using Pt disk and wire as working and counter electrode, Ag/Ag⁺ as reference electrode and Bu₄NClO₄ (0.1 M) as supporting electrolyte. Measurements were carried out at room temperature with a scan rate of 50 mV s⁻¹.

waves were observed at $E_{1/2} = -1.16$ and -1.44 V (Fig. 3). These waves can be assigned to the characteristic ring-based electrochemistry of phthalocyanines.²⁰ The position of the reduction waves and the absence of clear oxidation signals in the electrochemical window of the solvent are consistent with the electron-poor nature of the phthalocyanine core due to the presence of eight electron-withdrawing alkoxycarbonyl groups (see our earlier studies of metal-free phthalocyanine **1e** and also a communication by Torres, Guldi and co-workers on a palladium phthalocyanine bearing alkylsulfonfyl substituents).^{5,21} Finally, no measurable difference in reduction potentials was observed upon titration of the solution with metal-competing amine ligands (pyridine or Et_3N), thus not giving any evidence of the influence of aggregation on the redox potentials within the investigated concentration range.

3. Conclusion

We have described an efficient synthesis of ester-functionalized phthalonitriles via Pd-catalyzed two-fold cyanation of the corresponding dialkyl dichlorophthalates with $\text{Zn}(\text{CN})_2$ as a source of cyanide. Since phthalonitriles are used in the synthesis of some otherwise hardly accessible heterocyclic systems,²² reported by us, method for the preparation of functionalized dinitriles may serve as a convenient entry to such intermediates.

In addition, we have reported the one-pot synthesis of ester-functionalized zinc phthalocyanines from dichlorophthalates by Pd-catalyzed cyanation followed by in situ macrocyclization. To the best of our knowledge, this is the only example of such synthesis of Zn-phthalocyanine derivatives. Unfortunately, the yield of zinc phthalocyanines remained relatively low. Nevertheless, this method is of certain interest since it gives rapid access to functionalized metalated phthalocyanines in only two steps starting from commercial materials. This approach could be useful in the synthesis of other substituted zinc phthalocyanines from the corresponding *ortho*-dihalobenzenes, and one may expect that other type of functional groups will give better yields.

Due to large electron density of the central metal atom, liquid crystalline phthalocyanine **7e** is an interesting and useful object for the X-ray diffraction studies. Unlike for the metal-free analog bearing identical peripheral substituents, a number of higher order reflections are observed in the powder X-ray diffraction pattern of **7e**. This made possible the identification of slightly different LC mesophases. We plan to investigate by powder X-ray diffraction the miscibility of **7e** with other phthalocyanine materials and the morphology of such binary blends.

4. Experimental section

4.1. General

All chemicals were purchased from Aldrich or Acros and used without further purification unless stated otherwise. All

Pd-catalyzed reactions were performed in oven-dry glassware under dry Ar atmosphere. Dry *N,N*-dimethylacetamide was kept over 4 Å molecular sieves. Column chromatography: SiO_2 Kieselgel 60 (Macherey-Nagel, particle size 0.04–0.063 mm). TLC: precoated SiO_2 plates Kieselgel 60F₂₅₄ (Merck). ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker Avance 300 spectrometer at 25 °C; chemical shifts (δ) are given in parts per million relative to Me_4Si ; coupling constants (J) are given in hertz. Electron impact mass spectra (EIMS) were recorded on a Waters AutoSpec 6F instrument and matrix-assisted laser desorption/ionization mass spectra (MALDIMS) on a Waters QToF 2 instrument; m/z with the lowest isotopic mass are reported. IR spectra were recorded on a Shimadzu IR-470 instrument. Phase transition temperatures were determined by differential scanning calorimetry (Perkin–Elmer Diamond DSC) 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.

Powder X-ray diffraction measurements were performed on a Bruker D8 Advance diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418$ Å). All samples were prepared on thin pre-cleaned aluminum plates. Diffraction patterns were collected in the scattered angular range between 1.5° and 30° with the angular resolution of 0.02° per step and a typical counting time of 10 s per step, using the Bragg–Brentano geometry ($\theta/2\theta$ set-up). X-ray spectra are represented as the scattering intensity versus the wave-vector transfer $q = 4\pi \sin(\theta) \lambda^{-1}$ [$\text{\AA}^{-1}$]. The sample temperature was controlled within 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 $A = 0.785 \text{ mm}^2$, 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 an Ag/AgCl secondary electrode. All potentials were internally referenced to the ferrocene–ferrocinium (Fc/Fc^+) couple. All solutions were prepared in freshly distilled anhydrous and deaerated CH_2Cl_2 or THF containing 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ (TBAPF_6 , Fluka), which was recrystallized twice from ethanol and dried in vacuum prior to use.

4.2. Synthesis of diesters **5a–e**

Diethyl 4,5-dichlorophthalate **5a** has been prepared from the acid **4** according to the published procedure and its analytical data were identical to those published earlier.⁸ For homo-logs **5b–e**, we slightly modified the same method.

4.2.1. Dipentyl 4,5-dichlorophthalate (**5b**)

A mixture of acid **4** (20 mmol, 4.70 g), *n*-pentanol (**6b**, 10 mL, 90 mmol), H₂SO₄ (0.5 mL), and toluene (30 mL) was placed in a 100-mL round-bottom flask equipped with a Dean-Stark apparatus and heated to vigorous reflux for 15 h. The resulting mixture was cooled to room temperature, washed with H₂O (50 mL), 10% aqueous NaHCO₃ (20 mL), again H₂O (50 mL), and dried over MgSO₄. After evaporation of solvents, the residue was purified by chromatography on a short column of SiO₂, eluent hexane/CH₂Cl₂ 1:1. Yield 6.75 g (90%). Colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 0.92 (t, ³J_{H,H}=7.1 Hz, 6H), 1.30–1.40 (m, 8H), 1.68–1.78 (m, 4H), 4.29 (t, ³J_{H,H}=7.0 Hz, 4H), 7.88 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 13.9, 22.2, 27.9, 28.1, 66.3, 130.8, 131.7, 135.5, 165.6.

4.2.2. Dioctyl 4,5-dichlorophthalate (**5c**)

Prepared similarly to **5b** from *n*-octanol (**6c**, 7.8 mL, 50 mmol). Yield 75%. Colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 0.88 (t, ³J_{H,H}=6.9 Hz, 6H), 1.20–1.45 (m, 20H), 1.68–1.78 (m, 4H), 4.29 (t, ³J_{H,H}=7.0 Hz, 4H), 7.79 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 14.1, 22.6, 25.9, 28.4, 29.1, 29.2, 31.8, 66.4, 130.8, 131.8, 135.5, 165.6.

4.2.3. Didodecyl 4,5-dichlorophthalate (**5d**)

Prepared similarly to **5b** from *n*-dodecanol (**6c**, 9.3 g, 50 mmol). Yield 72%. Colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 0.88 (t, ³J_{H,H}=6.7 Hz, 6H), 1.20–1.45 (m, 36H), 1.66–1.78 (m, 4H), 4.29 (t, ³J_{H,H}=6.8 Hz, 4H), 7.79 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 14.0, 22.6, 25.8, 28.4, 29.2, 29.3, 29.45, 29.52, 29.57, 29.59, 31.9, 66.3, 130.8, 131.7, 135.4, 165.5.

4.2.4. Bis(2-butyloctyl)-4,5-dichlorophthalate (**5e**)

Prepared similarly to **5b** from alcohol **6e** (11.2 mL, 50 mmol) with the following amendment; after purification by chromatography the product, still containing the starting alcohol **6e** was partitioned between hexane (100 mL) and MeOH (100 mL). The upper hexane layer was separated and concentrated to give pure **5e**. Yield 78%. Colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 0.82–0.94 (m, 12H), 1.20–1.40 (m, 32H), 1.64–1.80 (m, 2H, CH), 4.20 (d, ³J_{H,H}=5.9 Hz, 4H), 7.77 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 13.98, 14.02, 22.6, 22.9, 26.6, 28.9, 29.6, 30.9, 31.2, 31.8, 37.2, 69.1, 130.8, 131.9, 135.4, 165.6.

4.3. Synthesis of dinitriles **3a–d**

4.3.1. Diethyl 4,5-dicyanophthalate (**3a**)

Diester **5a** (436 mg, 1.5 mmol), Pd₂(dba)₃ (55 mg, 0.06 mmol), dppf (66 mg, 0.09 mmol), Zn powder (20 mg, 0.3 mmol), and Zn(CN)₂ (210 mg, 1.8 mmol) were placed in a dry flask flushed with argon. Dry *N,N*-dimethylacetamide (6 mL) was added via syringe. The resulting mixture was heated at 120 °C for 2 h, then cooled to room temperature, and partitioned between H₂O (50 mL) and AcOEt (50 mL). The resulting biphasic system was filtered through Celite,

the organic layer was separated, and the aqueous layer was extracted with AcOEt (50 mL). The combined organic extracts were washed with H₂O (50 mL), dried over MgSO₄, and concentrated in vacuum. Column chromatography on SiO₂ (CH₂Cl₂) afforded 330 mg (81%) of **3a**. Colorless solid; mp 124–125 °C; IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3150 m, 3030 s, 2970 s, 2238 m (C≡N), 1735 s (CO), 1462 m, 1367 s, 1211 s, 1134 s, 1026 s, 932 m, 938 m, 854 m, 787 m; ¹H NMR (300 MHz, CDCl₃): δ 1.40 (t, ³J_{H,H}=7.1 Hz, 6H), 4.42 (q, ³J_{H,H}=7.1 Hz, 4H), 8.13 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 13.9, 63.1, 114.0, 118.0, 133.8, 136.4, 164.0; HREIMS: *m/z* calcd for C₁₄H₁₂N₂O₄ ([M]⁺): 272.0797; found: 272.0801.

4.3.2. Dipentyl 4,5-dicyanophthalate (**3b**)

Prepared similarly to **3a** from **5b** (563 mg, 1.5 mmol). Column chromatography on SiO₂ (CH₂Cl₂) afforded 442 mg (83%) of **3b**. Colorless solid; mp 67–71 °C; IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3040 m, 2950 s, 2845 s, 2239 m (C≡N), 1733 s (CO), 1462 m, 1396 m, 1379 m, 1299 s, 1247 s, 1211 s, 1137 s, 1008 m, 948 s, 898 m; ¹H NMR (300 MHz, CDCl₃): δ 0.92 (t, ³J_{H,H}=7.0 Hz, 6H), 1.30–1.42 (m, 8H), 1.68–1.80 (m, 4H), 4.35 (t, ³J_{H,H}=6.6 Hz, 4H), 8.12 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 13.8, 22.2, 27.9, 28.0, 67.2, 114.0, 118.0, 133.8, 136.5, 164.1; HREIMS: *m/z* calcd for C₂₀H₂₄N₂O₄ ([M]⁺): 356.1736; found: 356.1733.

4.3.3. Dioctyl 4,5-dicyanophthalate (**3c**)

Prepared similarly to **3a** from **5c** (690 mg, 1.5 mmol). Column chromatography on SiO₂ (hexane/AcOEt 10:1) afforded 493 mg (74%) of **3c**. Colorless solid; mp 44–46.5 °C; IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3035 w, 2945 s, 2905 s, 2835 s, 2237 m (C≡N), 1734 s (C=O), 1458 m, 1390 m, 1313 s, 1260 s, 1248 m, 1213 m, 1138 m, 935 m, 770 w, 720 w, 530 w; ¹H NMR (300 MHz, CDCl₃): δ 0.88 (t, ³J_{H,H}=6.9 Hz, 6H), 1.20–1.45 (m, 20H), 1.68–1.80 (m, 4H), 4.35 (t, ³J_{H,H}=6.8 Hz, 4H), 8.12 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 14.0, 22.6, 25.8, 28.4, 29.11, 29.14, 31.7, 67.3, 114.0, 118.0, 133.8, 136.5, 164.1; HREIMS: *m/z* calcd for C₂₆H₃₆N₂O₄ ([M]⁺): 440.2675; found: 440.2671.

4.3.4. Didodecyl 4,5-dicyanophthalate (**3d**)

Prepared similarly to **3a** from **5d** (857 mg, 1.5 mmol). Column chromatography on SiO₂ (hexane/AcOEt 10:1) afforded 596 mg (72%) of **3d**. Colorless solid; mp 65–65.5 °C; IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 2900 s, 2830 s, 2238 m (C≡N), 1734 s (C=O), 1453 m, 1306 m, 1258 m, 1199 m, 1133 m; ¹H NMR (300 MHz, CDCl₃): δ 0.88 (t, ³J_{H,H}=6.7 Hz, 6H), 1.20–1.45 (m, 36H), 1.68–1.80 (m, 4H), 4.35 (t, ³J_{H,H}=6.8 Hz, 4H), 8.12 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 14.1, 22.7, 25.8, 28.4, 29.2, 29.3, 29.47, 29.55, 29.59, 29.61, 31.9, 67.3, 114.0, 118.0, 133.8, 136.5, 164.1; HREIMS: *m/z* calcd for C₃₄H₅₂N₂O₄ ([M]⁺): 552.3927; found: 552.3916.

4.3.5. 2,3,9,10,16,17,23,24-Octakis(ethoxycarbonyl)-phthalocyanatozinc(II) (**7a**)

The same procedure as for the synthesis of **3a** from **5a** was used with the following amendment; the reaction mixture was

heated at 140 °C for 16 h. The same workup followed by column chromatography on SiO₂ (gradient from CH₂Cl₂ to CH₂Cl₂/AcOEt 1:1) afforded 59 mg (13%) of **7a**. Dark blue-green solid; ¹H NMR (300 MHz, CDCl₃+C₅D₅N): δ 1.67 (t, ³J_{H,H}=7.2 Hz, 24H, CH₃), 4.74 (d, ³J_{H,H}=7.2 Hz, 16H, CH₂COO), 9.90 (s, 8H, CH_{arom}); λ_{max} (CH₂Cl₂): 352, 617, 687. HRMALDIMS: *m/z* calcd for C₅₆H₄₈N₈O₁₆Zn ([M]⁺): 1152.2480; found: 1152.2500. IR (KBr) (ν_{max}/cm⁻¹): 2960 m, 1734 s (C=O), 1358 m, 1262 s, 1180 m, 1097 s, 1078 s, 1016 m, 750 m.

4.3.6. 2,3,9,10,16,17,23,24-Octakis(2-butyloctyl-1-oxy-carbonyl)phthalocyanatozinc(II), mixture of diastereoisomers (**7e**)

The same procedure as for the synthesis of **7a** from **5a** was used with the following amendment; after the reaction mixture was heated at 120 °C for 2 h, DBU (0.30 mL, 2 mmol) was added, the temperature was increased to 140 °C, and the heating was continued for 16 h. The same workup followed by column chromatography on SiO₂ (gradient from CH₂Cl₂ to CH₂Cl₂/AcOEt 10:1) afforded 85 mg (10%) of **7e**. Dark-green waxy solid; ¹H NMR (300 MHz, CDCl₃+C₅D₅N): δ 0.87 (t, ³J_{H,H}=7.0 Hz, 24H, CH₃), 1.02 (t, ³J_{H,H}=7.0 Hz, 24H, CH₃), 1.25–1.70 (m, 128H), 2.00–2.10 (m, 8H, CHCH₂COO), 4.55 (d, ³J_{H,H}=5.9 Hz, 16H, CH₂COO), 9.89 (s, 8H, CH_{arom}); ¹³C NMR (75 MHz, CDCl₃+C₅D₅N): δ 14.1, 14.2, 22.7, 23.2, 26.8, 29.1, 29.8, 31.2, 31.5, 31.9, 37.5, 69.4, 124.1, 133.9, 139.8, 154.1, 168.1; λ_{max} (ε, L cm⁻¹ mol⁻¹, CH₂Cl₂): 352 (8.81×10⁴), 617 (4.65×10⁴), 687 (2.79×10⁵). HRMALDIMS: *m/z* calcd for C₁₃₆H₂₀₈N₈O₁₆Zn ([M]⁺): 2273.5000; found: 2273.5037. IR (KBr) (ν_{max}/cm⁻¹): 2905 s, 2840 s, 1734 s (C=O), 1452 m, 1371 m, 1314 s, 1256 s, 1169 m, 1098 s, 1073 s, 1000 m, 746 m, 675 m.

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Supplementary data

Original ¹H and ¹³C NMR spectra, POM texture, additional powder X-ray data for **7e**; schematic representation of 2D lattices of Col_r mesophases with *P2gg* and *C2mm* symmetry.

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.03.004.

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