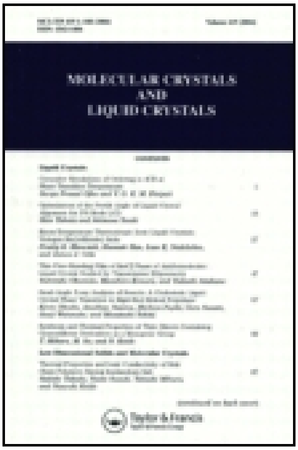

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Synthesis and Mesomorphism of Octaalkyl-Substituted Phenanthrene-9, 10-dionedioximato Complexes with Nickel, Palladium and Platinum

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Synthesis and Mesomorphism of Octaalkyl-Substituted Phenanthrene-9,10-dionedioximato Complexes with Nickel, Palladium and Platinum

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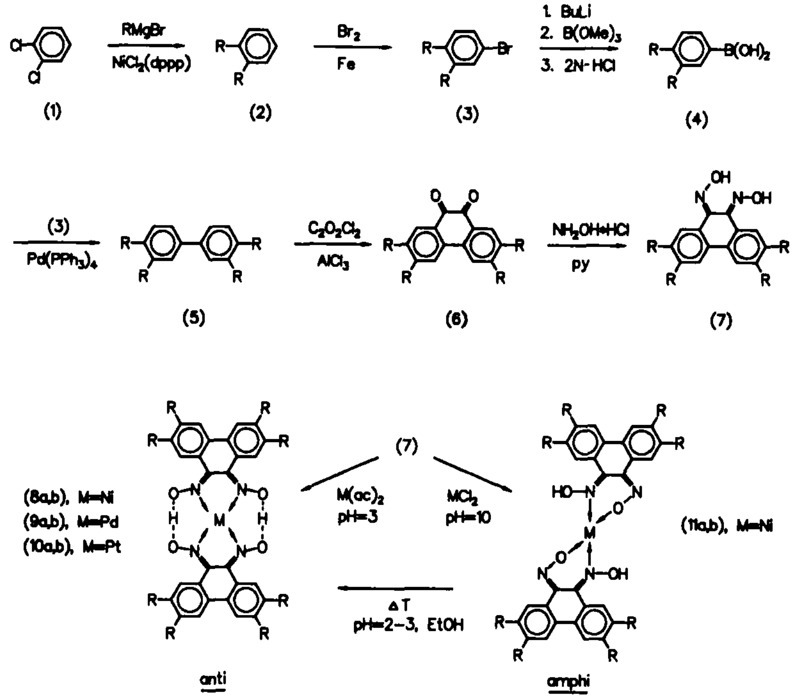
In this communication we describe the synthesis of 2,3,6,7-tetra-n-alkyl-substituted phenanthrene-9,10-dionedioximes (with n = hexyl and decyl) and their complexation to the metals nickel, palladium and platinum to yield the corresponding complexes as *amphi*- and *anti*-isomers. The thermal behavior of these complexes was investigated by polarizing microscopy, differential scanning calorimetry and X-ray diffraction. The *anti*-complexes form discotic rectangular disordered columnar (D_{rd}) and discotic hexagonal disordered columnar (D_{hd}) mesophases, whereas the *amphi*-isomers do not exhibit mesomorphism. The *amphi*-complexes can be isomerized to *anti*-complexes either thermally or by treatment under acidic conditions.

Keywords: Transition metal complexes, metallomesogens, discotic columnar mesophases.

1. INTRODUCTION

Liquid crystals composed of transition metal complexes promise to remarkably increase the range and scope of properties exhibited by conventional mesomorphic materials.[1] Dioximato-complexes with metals of the nickel-triad have been the subject of extensive investigations since they frequently crystallize with the formation of columnar stacks, leading to a chain of metal atoms perpendicular to the molecular planes.[2] One-dimensional metal-metal interactions could be the key for a number of interesting phenomena such as one-dimensional conductivity,[2b,3] high birefringence, or enhanced nonlinear optical response.[4] This phenomenon could be generated through the columnar superstructure present in discotic liquid crystals. Recently, Ohta and co-workers described the synthesis and mesomorphism of benzil-derived discotic columnar dioximato metal-complexes, which constitute the first examples of discotic columnar liquid crystals in the bis(dionedioximato) metal (II) system.[5] To further address this issue we have now developed a new synthetic approach to octaalkyl-substituted bis(phenanthrene-9,10-dionedioximato) complexes (**8–11**) with the metals nickel, palladium and platinum (herein abbreviated as M-Phen-C_nH_{2n+1}, with M = Ni, Pd, and Pt, n = 6 and 10) as shown in Scheme 1.



SCHEME 1 Synthesis of the M-Phen-C_nH_{2n+1} complexes (**8-11**), R = C_6H_{13} (a) and $C_{10}H_{21}$ (b).

2. RESULTS AND DISCUSSION

2.1 Synthesis

Amphi[6]-2,3,6,7-tetraalkylphenanthrene-9,10-dionedioxime (**7**) was prepared by reaction of the corresponding dione (**6**) with hydroxylamine hydrochloride in high yields. This dione could not be prepared from the corresponding benzil by oxidative coupling, a method highly efficient for the synthesis of the analogus tetraalkoxy-substituted phenanthrene-9,10-diones.[7] Our attempts to obtain the dione (**6**) under reductive conditions from the benzil using C_8K as reagent[8] were tedious and furnished very low yields only (5%), besides a large number of byproducts, which could only be removed by repeated column chromatography. The synthetic approach presented herein involves the palladium (0)-catalyzed Suzuki-coupling[9] of the arylbromide (**3**) with the arylboronic acid (**4**) which gives the biphenyl (**5**) in nearly quantitative yields. Biphenyl (**5**) is then converted by an intramolecular Friedel-Crafts reaction with oxalyl chloride to the phenanthrene-9, 10-dione (**6**). This two-fold Friedel-Crafts reaction proceeds in high yields, most likely induced by favorable electronic and steric conditions present in the tetrasubstituted biphenyls.[10] We found that complexation of the *amphi*-dioximes (**7**) with metal (II) salts (where metal = nickel, palladium and platinum) resulted in either *anti*- or *amphi*-metal (II) complexes (**8–11**), depending on the applied reaction conditions as shown in Scheme 1. The type of the formed isomer can be readily distinguished by the characteristic ^{1}H-NMR shifts of the oxime and aromatic protons, which differ significantly for the two isomers.[11] Complexation in acid media yields the *anti*-isomers, whereas under basic conditions formation of the *amphi*-isomers prevails. However, only nickel complexes could be isolated as pure isomers in the *amphi*-conformation, while the palladium and platinum analogues were already partly isomerized to the *anti*-isomers during complex formation. Identical observations were made for the analogou alkoxy-substituted complexes.[12] All *amphi*-complexes were readily isomerized to the thermodynamically favored *anti*-complexes, either thermally or by treatment under acidic conditions in various organic solvents (e.g. chloroform, benzene, or tetrahydrofuran).

2.2 Mesogenic behavior

The *anti*-complexes (**8–10**) melt to give birefringent fluid phases which display enantiotropic mesomorphic behavior, whereas the *amphi*-isomers (**11**) give an isotropic melt. Phase-transition temperatures and the corresponding enthalpy changes are summarized in Table 1. The width of the temperature range of mesomorphism is roughly side chain independent at 85-90°C, and the melting and clearing points both decrease as the side chain length increases.

DSC analysis of the decyl-substituted complexes (**8b–10b**) shows a large enthalpy (68.1–73.7 kJ/mol) for the crystal-to-liquid crystal transition at temperatures between 126.0 and 130.5°C, as well as several enantiotropic crystal-to-crystal transitions with

TABLE 1

Phase transition temperatures and corresponding enthalpy changes ΔH_t (kJ/mol).

Compound	Phase $\dfrac{T_t\,(^\circ\mathrm{C})}{[\Delta H_t\ (\mathrm{kJ/mol})]}$ Phase
(**8a**) anti-Ni-Phen C_6H_{13}:	$K_1 \underset{[23.0]}{\overset{17.2}{\rightleftharpoons}} K_2 \underset{[63.5]}{\overset{167.0}{\rightleftharpoons}} D_{rd} \underset{[a]}{\overset{228.0}{\rightleftharpoons}} D_{hd} \underset{[6.0]}{\overset{253.1}{\rightleftharpoons}} i$
(**9a**) anti-Pd-Phen C_6H_{13}:	$K_1 \underset{[20.9]}{\overset{74.7}{\rightleftharpoons}} K_2 \underset{[50.2]}{\overset{163.1}{\rightleftharpoons}} D_{rd} \underset{[a]}{\overset{227.0}{\rightleftharpoons}} D_{hd} \xrightarrow{255}$ i (Decomp.)
(**10a**) anti-Pt-Phen C_6H_{13}:	$K_1 \underset{[29.0]}{\overset{64.9}{\rightleftharpoons}} K_2 \underset{[23.9]}{\overset{166.1}{\rightleftharpoons}} D_{rd} \underset{[a]}{\overset{227.5}{\rightleftharpoons}} D_{hd} \xrightarrow{250}$ i (Decomp.)
(**11a**) amphi-Ni-Phen C_6H_{13}:	$K_1 \underset{[40.4]}{\overset{125.4}{\rightleftharpoons}} i$
(**8b**) anti-Ni-Phen $C_{10}H_{21}$:	$K_1 \underset{[6.6]}{\overset{6.2}{\rightleftharpoons}} K_2 \underset{[17.2]}{\overset{84.0}{\rightleftharpoons}} K_3 \underset{[16.9]}{\overset{104.4}{\rightleftharpoons}} K_4 \underset{[71.8]}{\overset{130.5}{\rightleftharpoons}} D_{hd} \underset{[5.2]}{\overset{214.1}{\rightleftharpoons}} i$
(**9b**) anti-Pd-Phen $C_{10}H_{21}$:	$K_1 \underset{[12.8]}{\overset{26.1}{\rightleftharpoons}} K_2 \underset{[11.8]}{\overset{69.9}{\rightleftharpoons}} K_3 \underset{[15.5]}{\overset{106.1}{\rightleftharpoons}} K_4 \underset{[73.7]}{\overset{128.0}{\rightleftharpoons}} D_{hd} \underset{[5.6]}{\overset{214.4}{\rightleftharpoons}} i$
(**10b**) anti-Pt-Phen $C_{10}H_{21}$:	$K_1 \underset{[5.6]}{\overset{26.0}{\rightleftharpoons}} K_2 \underset{[13.3]}{\overset{98.2}{\rightleftharpoons}} K_3 \underset{[68.1]}{\overset{126.0}{\rightleftharpoons}} D_{hd} \underset{[7.7]}{\overset{215.8}{\rightleftharpoons}} i$
(**11b**) amphi-Ni-Phen $C_{10}H_{21}$:	$K_1 \underset{[54.9]}{\overset{90.3}{\rightleftharpoons}} i$

[a] no enthalpy change detectable by DSC analysis, K_i, i = 1, 2, 3, 4: various crystalline modifications, D_{rd}: disordered rectangular columnar mesophase, D_{hd}: disordered hexagonal columnar mesophase, i: isotropic melt.

significantly lower transition enthalpies (5.6–17.2 kJ/mol). The low enthalpy (5.2–7.7 kJ/mol) for the liquid crystal-to-isotropic transition is typical for discotic columnar mesogens. The textures of the liquid crystalline phases as viewed under a polarizing microscope are essentially identical for all of these complexes and can be best described as fan shaped or focal conic (Fig. 1a), frequently observed for discotic hexagonal disordered (D_{hd}) mesogens.[13] X-ray diffraction of the mesophases (Fig. 2) confirms that the columns pack in a hexagonal array with liquid-like order within the columns. The X-ray pattern shows four narrow reflections at small scattering angles, which could be asigned to (100), (110), (200) and (210) in a two-dimensional lattice, as well as a diffuse band at $d = 4.4$ Å, which corresponds to liquid correlations between molten hydrocarbon side chains. The lattice constant a was determined to 25.6 Å (**8b**), 25.4 Å (**9b**), and 25.4 Å (**10b**), respectively.

The hexyl-substituted complexes (**8a–10a**) exhibit relatively high clearing points (250–255°C) which are accompanied by significant decomposition for the palladium and platinum derivatives. DSC analysis shows also a crystal-to-crystal phase-transition with substantial enthalpies (20.9–29.0 kJ/mol) for each of these complexes as well as the crystal-to-liquid crystal transition at temperatures between 163.1 and 167.0°C. The melting enthalpy for the platinum complex (**10a**) is significantly smaller in comparison to its nickel and palladium analogues (**8a**) and (**9a**), although all these complexes demonstrate essentially identical mesomorphic behavior. Polarizing microscopical studies for these complexes revealed a more complex mesomorphic behavior than indicated by DSC analysis. When slowly cooled from the isotropic melt, the complexes revealed a more complex mesomorphic behavior than indicated by DSC analysis. When slowly cooled from the isotropic melt, the complexes (**8a–10a**) display fan shaped textures (Fig. 1b) identical to those observed for the decyl-substituted derivatives,

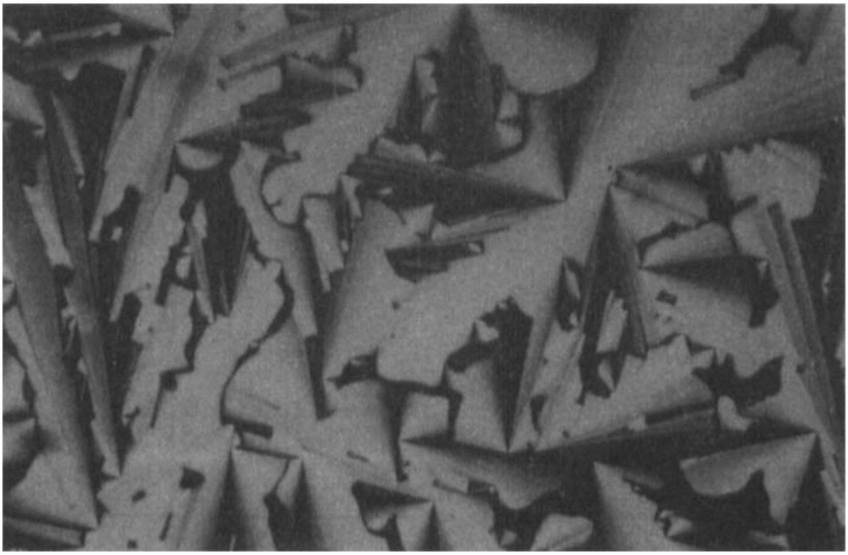


FIGURE 1a Polarizing microscopical image of the Ni-Phen-$C_{10}H_{21}$ complex (**8b**) at 160°C. See color plate IV.

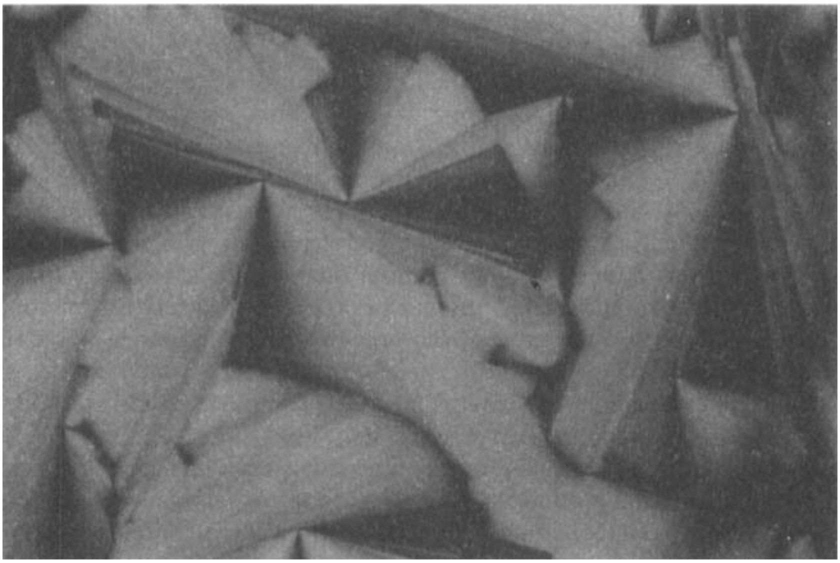


FIGURE 1b Polarizing microscopical image of the Ni-Phen-C_6H_{13} complex (**8a**) at 245°C. See color plate V.

FIGURE 1c Polarizing microscopical image of the Ni-Phen-C_6H_{13} complex (**8a**) at 228°C. See color plate VI.

indicating a hexagonal columnar structure. On further cooling, the texture changed at about 228°C to banded or broken fan shaped features (Fig. 1c). This texture combined with an analysis of the directional nature of the extinction brushes indicates a tilted rectangular structure.[13a,14] This enantiotropic transition could not be detected in DSC studies. The mosaic texture remains unchanged towards lower temperatures until transition to the crystalline phase occurs at about 130°C.

X-ray diffraction studies (Fig. 3) of the low-temperature mesophases confirm that the columns pack in a rectangular array with liquid-like order within the columns (D_{rd}). The five narrow reflections in the low angle region correspond to (200), (110), (310), (020) and (400) in a two-dimensional rectangular array with lattice constants $a = 36.9$ Å, $b = 20.7$ Å, (**8a**), $a = 37.2$ Å, $b = 20.8$ Å, (**9a**) and $a = 37.1$ Å, $b = 21.0$ Å, (**10a**), respectively. X-ray diffraction studies of the high temperature mesophases were not possible due to slow thermal decomposition of the complexes. However, polarizing microscopy clearly identifies them as discotic hexagonal disordered (D_{hd}) mesophases.

Interestingly, the lattice constants of the complexes presented herein are about 3–4 Å shorter compared with the values observed for the structurally similar bis[1, 2-bis(3, 4-dialkylphenyl) ethanedione dioximato] metal (II) complexes (Fig. 4) with identical chain lengths, which also form (D_{hd}) mesophases.[15]

However, the aromatic cores in these complexes possess a high degree of flexibility due to potential rotation around the phenylic carbon-carbon bond. We believe that the difference of the intercolumnar distance hints to a tilted columnar stacking for the complexes (**8–10**), propagated by the increased rigidity of their aromatic core. This arrangement in tilted stacks is a motif well known in the crystalline state of

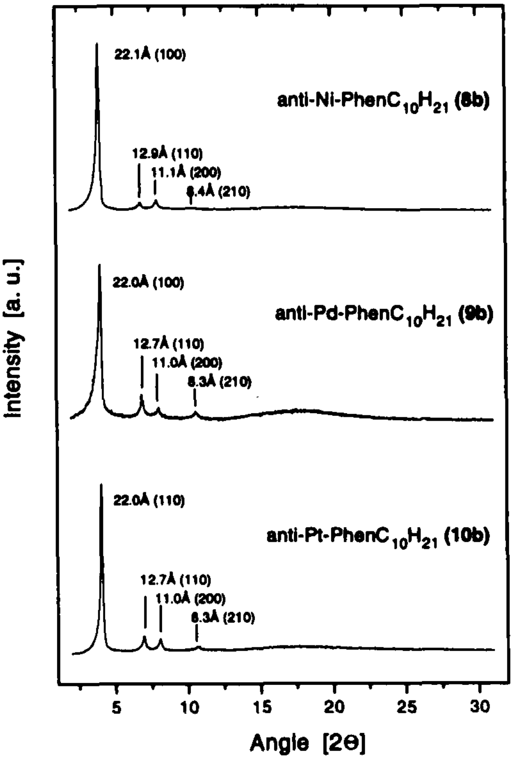


FIGURE 2 X-ray diffraction pattern of the complexes **8b–10b** at 130°C.

rigid aromatic cores[16] and was recently also verified in hexagonal columnar Phthalocyaninato-[17,18] and bis (tetraalkoxy phenanthrene-9,10-dionedioximato)-metallomesogens.[12] The hexagonal packing in these systems is achieved by complete rotational disorder about the column axis.

2.3 UV/Vis-Spectroscopy

Metal (II) bis(dionedioximato) complexes have long been the subject of spectroscopic studies, largely as a result of the unusual solid-state optical properties they commonly display relative to their solution spectra.[2] A sharp absorption band usually observed in the crystalline state has been assigned to the optical $nd \rightarrow (n+1)p$ interband transition. This lowest-energy absorption corresponds to one-dimensional metal-metal interactions which arise from the columnar stacking frequently observed for these complexes. The position of this transition is very sensitive to the one-dimensional metal-metal stacking distance, leading to a large blue shift with increasing distance. Ohta and co-workers recently reported the electronic spectra of mesomorphic bis (dionedioximato) metal (II) complexes, which display *mesomorphic thermochroism.*[5]

Figure 5 depicts the UV/Vis-spectra of thin cast-films in the crystalline and liquid crystalline phase as well as in chloroform solution ($c = 1.0\,g/l$) for the *anti*-M-Phen-

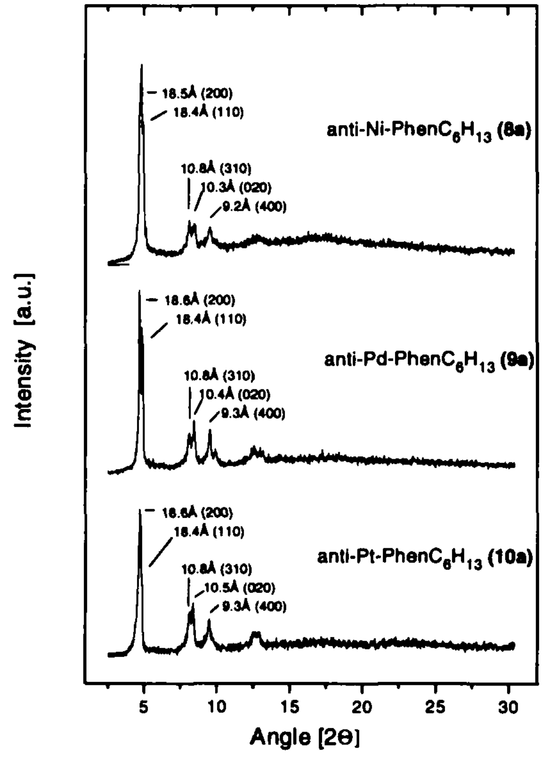


FIGURE 3 X-ray diffraction pattern of the complexes **8a–10a** at 190°C.

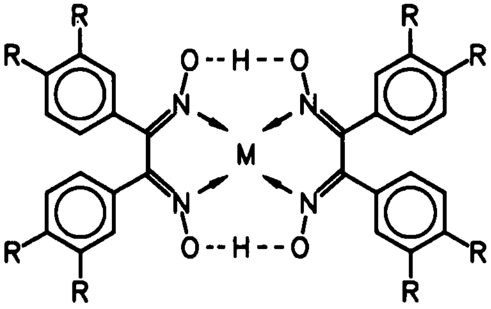


FIGURE 4 Bis [1,2-bis(3,4-dialkylphenyl) ethanedione dioximato] metal (II) complexes.

$C_{10}H_{21}$ complexes (**8a-10a**). The low-energy transitions for these complexes are assigned to metal-to-ligand charge-transfer bands (MLCT: B_{2u} or B_{3u}), which are reported for microcrystalline bis(diphenyldioximato) and bis(benzoquinone dioximato) complexes at similar wavelengths.[19,20] This assignment is substantiated by the fact that the spectral appearance is essentially identical in the crystalline and liquid-crystalline phase as well as in solution. Dilution of the chloroform solutions by a factor of 100 ($c = 0.01$ g/l) does not affect the absorption coefficient, excluding the possibility that this band arises from aggregates in solution. The slight blue-shift of the nickel-complex in solution might be explained by increased solvation effects. The high-energy transitions around 300 nm for each of the complexes represent π-π^* transitions in the ligand. We assume that the absence of an absorption band representing one-dimensional intermetallic interactions is due to a significantly enlarged metal-metal distance, originated by the proposed tilted columnar arrangement.

3. SUMMARY

We have synthesized and characterized two series of octaalkyl-substituted bis (phenanthrene-9, 10-dionedioximato) complexes with the metals nickel, palladium and platinum. Depending on the reaction conditions applied we could obtain either the *anti-* or *amphi*-isomer of the complexes. The *anti*-isomers form enantiotropic discotic columnar mesophases, whereas the *amphi*-isomers do not exhibit mesomorphism. All *amphi*-complexes can be isomerized to *anti*-complexes, either thermally or by treatment under acidic conditions in various organic solvents. Assignment of the phases has been made on the basis of polarizing microscopy, differential scanning calorimetry and X-ray diffraction. The comparison with structurally similar complexes and recent observations for other metallomesogens with rigid aromatic cores suggests a tilted columnar arrrangement. This assumption is further substantiated by the absence of the optical $nd \rightarrow (n+1)p$ interband transition in the electronic spectra. The mesomorphic behavior of the complexes presented herein is similar to that observed for the octaalkoxy-substituted analogues,[12] while the width of the temperature range of mesomorphism is reduced by 50°C for the alkyl-substituted derivatives. However, in some other related examples of discotic columnar metallomesogens, liquid crystallinity is completely

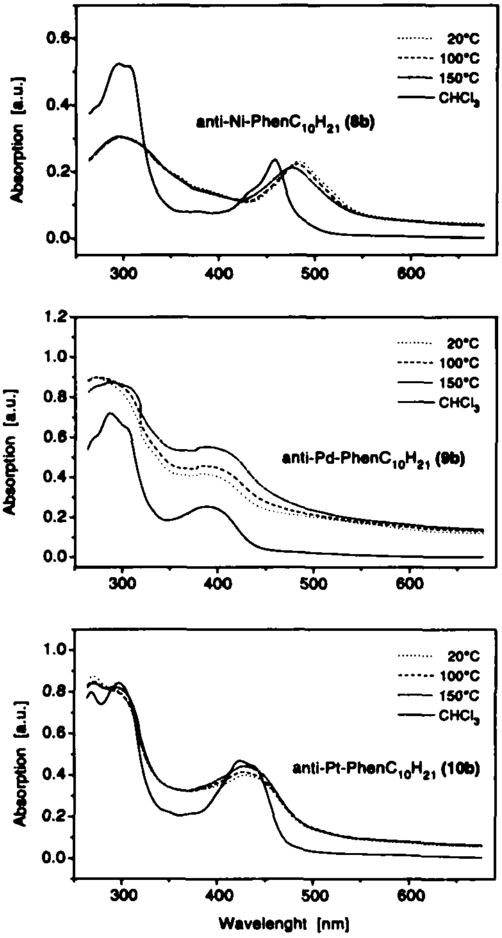


FIGURE 5 UV/Vis-spectra of the complexes **8b–10b**.

suppressed when alkoxy chains are substituted by alkyl chains.[13b] The tetraalkyl-substituted phenanthrene-9,10-diones presented in this work constitute potential precursors for a variety of other metallomesogens such as dithiolene-,[10,21] porphyrazine-[22] and phthalocyaninato-[23] complexes.

EXPERIMENTAL SECTION

Materials and Methods

Tetrakis (triphenylphosphine) palladium (0), $Pd(PPh_3)_4$ was synthesized according to a described procedure.[24] Anhydrous carbon disulfide was purchased from Aldrich and used without further purification. Toluene and tetrahydrofuran were purified and degassed by standard procedures prior to use. Column chromatography was performed on silica gel (230–400 mesh, Merck). NMR spectra were recorded on a Brucker AX-300 using $CDCl_3$ as a solvent and internal standard. Mass spectra were measured on a VG ZAB 2-SE-FPD. Elemental analyses were carried out at the Analytical Laboratory of the Department of Organic Chemistry at University of Mainz. Transition temperatures and enthalpy changes were determined with a Mettler DSC 30 with a 5 K/min scan rate. Microscopic observations of the textures were made using a Leitz Axiophot polarizing microscope equipped with a Linkam THM 600 hot stage and a TMS 90 thermal control unit. X-ray diffraction data were collected on a Siemens D 500 diffractometer with Ni-filtered Cu K_α radiation.

Following, we describe the synthesis of the n-decyl-substituted derivatives. The n-hexyl-derivatives were prepared in analogous manner.

1,2-Di-n-decylbenzene (2b)

2.5 equiv. Decyl magnesium bromide (245.3 g, 1.0 mol) in 500 mL ether were slowly added to an ice-cooled and stirred mixture of 58.8 g (400 mmol) 1,2-dichlorobenzene and 250 mg (0.4 mmol) Ni(dppp) Cl_2 in 600 mL dry ether under argon. The mixture was then refluxed for 48 h, cooled to 0°C and carefully quenched with 200 mL water, followed by addition of 300 mL 2 N HCl. After separation of the layers, the aqueous medium was extracted with ether and the combined organic layers were washed with water, dried ($MgSO_4$) and concentrated *in vacuo*. Distillation through a Vigreux column under reduced pressure yielded 96.1 g (67%) of a colorless liquid. bp. 145°C (0.02 mm Hg); ^{1}H-NMR δ 7.15 (broad *s*, 2H), 2.63 (*t*, 2H, J = 7.92 Hz), 1.66-1.58 (*m*, 2H), 1.42-1.20 (*m*, 14H), 0.92 (*t*, 3H, J = 6.70 Hz); ^{13}C-NMR δ 140.56, 129.10, 125.70, 32.75, 31.96, 31.38, 29.85, 29.68, 29.61, 29.40, 22.72, 14.12; FD m/z (relative intensity) 358 (M^+, 100). Anal. Calcd for $C_{26}H_{46}$: C, 87.07; H, 12.93. Found: C, 87.16; H, 12.88.

3,4-Di-n-decyl-1-bromobenzene (3b)

1.05 equiv. Bromine (9.40 g, 58.60 mmol) in 50 ml dichloromethane were slowly added to a stirred mixture of 20.0 g (55.80 mmol) 1,2-di-n-decylbenzene (**2b**) and 30 mg iodine in 250 ml dichloromethane at -10°C under strict exclusion of light. The mixture was then stirred for 12 h at -10°C, followed by addition of a solution of 10 g sodium dithionate in 200 ml water. After separation of the layers, the aqueous medium was extracted with ether and the combined organic layers were washed with water, dried ($MgSO_4$) and concentrated *in vacuo*, to yield 21.3 g (87.2%) of a yellow oil. ^{1}H NMR spectroscopy shows the desired product in a purity of more than 90%, as well as traces of edduct and dibrominated material. This material was used without further purification. ^{1}H-NMR δ 7.25 (*d*, 1H, J = 2.14 Hz), 7.20 (*dd*, 1H, J = 8.13 Hz, J = 2.14 Hz), 6.97 (*d*, 1H, J = 8.13 Hz), 2.54 (*t*, 2H, J = 7.76 Hz), 2.50 (*t*, 2H, J = 7.54 Hz), 1.56-1.48 (*m*, 4H), 1.31-1.24 (*m*, 28H), 0.87 (*t*, 6H, J = 46.76 Hz); ^{13}C-NMR δ 142.92, 139.50, 131.76, 130.75, 128.61, 119.25, 32.52, 32.19, 31.91, 31.11, 29.63, 29.51, 29.35, 22.69, 14.11; FD m/z (relative intensity) 436 (M^+, 100). Anal. Calcd for $C_{26}H_{45}$ Br: C, 71.37; H, 10.36. Found: C, 71.41; H, 10.54.

3,4-Di-n-decylphenylboronic acid (4b)

50 mL (80.0 mmol) of a 1.6 M solution n-butyl lithium in hexane were slowly added to a stirred solution of 26.3 g (60.0 mmol) 3,4-di-n-decyl-1-bromobenzene (**3b**) in 150 ml ether at 0°C under argon. The mixture was allowed to warm to ambient temperature and was stirred for another 2 h. This solution was transferred into a dropping funnel and added to a cooled (− 60°C) solution of 20.8 g (200 mmol) trimethyl borate in either, and was then stirred for 12 h at room temperature. After hydrolysis with aqueous HCl (2N, 300 ml), the layers were separated and the aqueous medium was twice extracted with ether. The combined organic layers were washed with water, dried ($MgSO_4$) and concentrated under reduced pressure to obtain a viscous tan oil, which was subjected to column chromatography (silica gel). 1,2-Di-n-decylbenzene and other byproducts were removed with dichloromethane, followed by elution of the desired product with *tert*-butylmethylether. Evaporation of the solvent yielded 6.3 g (27%) of a colorless oil, which slowly solidified. ^{1}H-NMR δ 7.98 (*d*, 1H, J = 7.95 Hz), 7.97 (*s*, 1H), 7.27 (*d*, 1H, J = 7.95 Hz), 2.70 (*t*, 2H, J = 8.44 Hz), 2.68 (*t*, 2H, J = 8.49 Hz), 1.71 – 1.55 (*m*, 4H), 1.45-1.18 (*m*, 28H), 0.88 (*t*, 3H, J = 6.54 Hz), 0.87 (*t*, 3H, J = 6.96 Hz); ^{13}C-NMR δ 145.58, 140.07, 136.48, 133.13, 128.87, 33.05, 32.75, 31.92, 31.34, 31.20, 29.81, 29.64, 29.37, 22.69, 14.11; FD m/z (relative intensity) 401 (M^+, 100). Anal. Calcd for $C_{26}H_{47}BO_2$: C, 77.60; H, 11.77. Found: C, 77.38; H, 11.99.

3,3′,4,4′-Tetra-n-decylbiphenyl (5b)

A mixture of 6.0 g (13.7 mmol) 3,4-di-n-decyl-1-bromobenzene (**3b**), 6.0 g (15.0 mmol) 3,4-di-n-decylphenylboronic acid (**4b**), and 160 mg (0.140 mmol) Pd $(PPh_3)_4$ was refluxed in the heterogeneous system toluene (50 ml), THF (30 ml), 2M K_2CO_3 (90 ml) for 48 h with vigorous stirring. A second portion of 160 mg (0.140 mmol) Pd $(PPh_3)_4$ was added to the reaction mixture after 24 h. After cooling to room temperature the layers were separated, the aqueous medium was extracted with ether. The combined organic layers were washed with water, dried over $MgSO_4$, and concentrated under reduced pressure to yield a dark viscous oil. Final purification was achieved by column chromatography (silica gel/dichloromethane) to provide 8.9 g (91%) of a yellow highly viscous oil. ^{1}H-NMR δ 7.33 (*d*, 1H, J = 1.96 Hz), 7.31 (*dd*, 1H, J = 8.25 Hz, J = 1.96 Hz), 7.16 (*d*, 1H, J = 8.25 Hz), 2.63 (*t*, 2H, J = 7.91 Hz), 2.60 (*t*, 2H, J = 7.88 Hz), 1.62 – 1.52 (*m*, 4H), 1.40-1.21 (*m*, 28H), 0.87 (*t*, 6H, J = 6.65 Hz); ^{13}C-NMR δ 140.80, 139.31, 138.83, 129.43, 127.82, 124.35, 32.95, 32.44, 31.94, 31.46, 31.38, 29.86, 29.66, 29.60, 29.38, 22.70, 14.11; FD m/z (relative intensity) 715 (M^+, 100). Anal. Calcd for $C_{52}H_{90}$: C, 87.32; H, 12.68. Found: C, 87.09; H, 12.76.

3,3′,4,4′-Tetra-n-decylphenanthrene-9,10-dione (6b)

Glassware used in this synthesis was dried thoroughly prior to use. To a mechanically stirred suspension of 4.0 g (6.0 mmol) 3,3′, 4,4′-tetra-n-decylbiphenyl (**5b**) and 1.87 g (14.0 mmol) aluminum chloride in 200 ml of carbon disulfide at 0°C was slowly added a solution of 1.90 g (15.0 mmol) oxalyl chloride in 30 ml carbon disulfide under a constant stream of argon. Stirring was continued for 14 h. The resulting red mixture was poured onto 300 ml ice and the orange organic phase was separated. The aqueous medium was extracted with dichloromethane and the combined organic layers were washed with water, dried ($MgSO_4$) and concentrated *in vacuo*. Recrystallization from acetone yielded 3.2 g of an orange solid. Final purification was achieved by column (silica gel/dichloromethane) to provide 2.91 g (64%) of an orange solid, mp. 84°C; ^{1}H-NMR δ 7.90 (*s*, 1H); 7.65 (*s*, 1H), 2.69 (*t*, 2H, J = 7.89 Hz), 2.61 (*t*, 2H, J = 7.91 Hz), 1.61-1.53 (*m*, 4H), 1.32-1.25 (*m*, 28H), 0.87 (*t*, 6H, J = 6.73 Hz); ^{13}C-NMR δ 180.77, 150.05, 142.33, 133.87, 131.11, 129.10, 124.42, 33.63, 32.28, 31.94, 30.88, 29.82, 29.66, 29.55, 29.37, 22.71, 14.11; FD m/z (relative intensity) 769 (M$^+$, 100). Anal. Calcd for $C_{54}H_{88}O_2$: C, 84.31; H, 11.53. Found: C, 84.33; H, 11.62.

amphi-3,3',4,4'-Tetra-n-decylphenanthrene-9,10-dionedioxime (7b)

A solution of 2.50 g (3,25 mmol) 3,3'4,4'-tetra-n-decylphenanthrene-9,10-dione (**6b**) and 2.80 g (40.0 mmol) hydroxylamine in 50 ml pyridine was stirred at 80°C until the color has turned to pale yellow (48 h). Upon cooling to room temperature 50 ml water were added. The yellow solid which precipitated was recovered by filtration through a Büchner funnel, washed with water and dried *in vacuo* to yield 2.42 g (93%) of a yellow solid, mp. 84°C, ^{1}H-NMR δ 8.71 (*s*, 1H); 7.90 (*s*, 1H), 7.74 (*s*, 1H), 7.65 (*s*, 1H), 2.71-2.58 (*m*, 8 Hz), 1.61-1.53 (*m*, 8H), 1.41-1.19 (*m*, 56H), 0.86 (*t*, 12H, J = 6.75 Hz); ^{13}C NMR δ 147.20, 145.20, 143.23, 142.87, 141.46, 139.96, 133.00, 131.80, 128.72, 126.74, 125.34, 124.16, 123.54, 121.81, 33.29, 33.09, 32.64, 33.09, 32.64, 31.91, 31.38, 31.17, 29.78, 29.64, 29.55, 29.34, 22.68, 14.10; FD m/z (relative intensity) 799 (M$^+$, 100). Anal. Calcd for $C_{54}H_{90}O_2$: C, 81.15; H, 11.35. Found: C, 80.98; H, 11.12.

anti-Bis(3,3',4,4'-Tetra-n-decylphenanthrene-9,10-dionedioximato)Ni(II) (8b)

A suspension of 500 mg (0.63 mmol) *amphi*-3,3',4,4'-tetra-n-decylphenanthrene-9,10-dionedioxime (**7b**) and 78.4 mg (0.32 mmol) Ni (acetate)$_2$. 4H$_2$O in 60 ml ethanol was refluxed for 8 h under argon at PH 3 (HCl). The red precipitate recovered by filtration through a Büchner funnel was washed with water and methanol and dried *in vacuo*. Final purification was achieved by column chromatography on silica gel with chloroform as eluent to yield 438 mg (84%) of a red solid. ^{1}H-NMR δ 18.76 (*s*, 1H); 9.26 (s, 2H), 7.66 (*s*, 2H), 2.56 (*m*, 8H), 1.61-1.54 (*m*, 8H), 1.41-1.22 (*m*, 56H), 0.86 (*t*, 6H, J = 6.56 Hz); ^{13}C-NMR δ 145.83, 144.25, 141.26, 131.33, 130.22, 123.60, 122.83, 33.37, 32.86, 31.94, 31.37, 31.15, 29.96, 29.89, 29.70, 29.2, 29.38, 22.70, 14.11; FAB-MS m/z (relative intensity) 1653.3 (M$^+$, 100). Anal. Calcd for $C_{108}H_{178}N_4O_4Ni$: C, 78.37; H, 10.84; Ni, 3.55. Found: C, 78.54; H, 10.66; Ni, 3.41.

anti-Bis(3,3',4,4'-Tetra-n-decylphenanthrene-9,10-dionedioximato Pd (II) (9b)

This complex was prepared analogously to (**8b**), using *amphi*-3,3',4,4'-tetra-n-decylphenanthrene-9,10-dionedioxime (**7b**) and $PdCl_2$ as starting materials. Orange solid (73%). ^{1}H-NMR δ 9.22 (*s*, 2H); 7.64 (*s*, 2H), 2.56 (*m*, 8H), 1.62-1.54 (*m*, 8H), 1.43-1.20 (*m*, 56H), 0.87 (*t*, 6H, J = 6.76 Hz); ^{13}C-NMR δ 146.53, 143.89, 141.12, 130.62, 129.70, 123.39, 123. 19, 33.35, 32.87, 31.96, 31.28, 31.10, 30.05, 29.95, 29.73, 29.66, 29.42, 22.71, 14.11; FAB-MS m/z (relative intensity) 1701.3 (M^+, 100). Anal. Calcd for $C_{108}H_{178}N_4O_4Pd$: C, 76.17; H, 10.53; Pd, 6.25. Found: C, 76.01; H, 10.62; Pd, 6.21.

anti-Bis(3,3′,4,4′-Tetra-n-decylphenanthrene-9,10-dionedioximato)Pt (II) (10b)

This complex was prepared analogously to (**8b**), using *amphi*-3,3′,4,4′-tetra-n-decylphenanthrene-9,10-dionedioxime(**7b**) and $PtCl_2$ as starting materials. Red solid (77%). ^{1}H-NMR δ 9.23 (*s*, 2H); 7.65 (*s*, 2H), 2.56 (*m*, 8H), 1.63-1.52 (*m*, 8H), 1.43-1.20 (*m*, 56H), 0.87 (*t*, 6H, J = 6.67 Hz); ^{13}C-NMR δ 147.80, 144.21, 141.24, 130.58, 129.81, 123.51, 123.35, 33.42, 32.88, 31.95, 31.30, 31.15, 30.01, 29.93, 29.72, 29.66, 29.41, 22.71, 14.11; FAB-MS m/z (relative intensity) 1790.4 (M^+, 100). Anal. Calcd for $C_{108}H_{178}N_4O_4Pt$: C, 72.40; H, 10.01; Pt, 10.89. Found: C, 72.12; H, 9.87; Pt, 10.52.

amphi-Bis(3,3′,4,4′-Tetra-n-decylphenanthrene-9,10-dionedioximato)Ni(II) (11b)

78.4 mg (0.32 mmol) $NiCl_2 \cdot 6H_2O$ were added to a suspension of 500 mg (0.63 mmol) *amphi*-3,3′,4,4′-tetra-n-decylphenanthrene-9,10-dionedioxime (**7b**) and 25 mg (0.63 mmol) sodium hydroxide in 50 ml methanol. The mixture was then stirred for 6 h at 50°C under argon. The red precipitate was recovered by filtration through a Büchner funnel, washed with water and methanol and dried *in vacuo*. Column chromatography on silica gel with dichloromethane as eluent yielded 438 mg (84%) of a red solid. This *amphi*-complex could be readily isomerized to the *anti*-isomer, either thermally (6 h at 160°C) or simply by stirring in a chloroform solution under addition of 0.1 ml diluted HCl (10 min, 50°C). ^{1}H-NMR δ 11.89 (*s*, 1H); 8.84 (*s*, 1H), 7.92 (*s*, 1H), 7.76 (*s*, 1H), 7.70 (*s*, 1H), 2.73-2.59 (*m*, 8H), 1.61-1.54 (*m*, 8H), 1.41-1.22 (*m*, 56H), 0.86 (*t*, 6H, J = 6.53 Hz); ^{13}C-NMR δ 145.66, 144.10, 142.13, 141.61, 139.50, 134.91, 132.86, 132.29, 127.54, 126.49, 125.09, 124.14, 123.27, 121.05, 33.36, 33.06, 32.82, 32.69, 31.93, 31.44, 31.11, 31.05, 30.42, 29.67, 29.37, 22.70, 14.11; FAB-MS m/z (relative intensity) 1653.3 (M^+, 100). Anal. Calcd for $C_{108}H_{178}N_4O_4Ni$: C, 78.37; H, 10.84; Ni, 3.55. Found: C, 78.31; H, 10.99; Ni, 3.27.

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