Columnar mesophases from half-discoid platinum cyclometalated metallomesogens†‡

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A series of liquid crystals have been synthesized and studied based upon mononuclear *ortho*-platinated rod-like heteroaromatic and 1,3-diketonate ligands. The liquid crystalline properties of these molecules were investigated using polarized light optical microscopy, differential scanning calorimetry, single crystal X-ray diffraction, and powder X-ray diffraction. Increasing the number of alkyl chains attached to the 1,3-diketonate units resulted in a transition from lamellar (SmA) to hexagonal columnar phases ($\mathrm{Col_h}$). The 2-thienylpyridine units were previously unexplored in metallomesogenic complexes and these studies extend the utility of *ortho*-platinated 2-phenylpyridines and 2-thienylpyridines to produce columnar liquid crystalline phases. The platinum complexes all display photoluminescence and are of interest for electrooptical applications.

Introduction

The design of molecule-based materials requires the controlled assembly of specific superstructures that transform discrete molecular properties into collective material properties. Liquid crystalline (mesomorphic) materials are excellent examples of designed supermolecular materials, and the cooperative physical properties of these materials have led to numerous technological applications.[1] The continued extension of liquid crystal science to additional technologies requires new types of mesomorphic materials that integrate novel structural elements and physical properties. To this end, mesogenic transition metal complexes[2] (metallomesogens) combine attractive optical and electronic properties with the fluidity, self-assembly, and self-healing properties of liquid crystals. The diversity of promesogenic organic structures that can be combined with the different geometries provided by the metals, allows access to a virtually unlimited number of unconventional functional mesomorphic materials. We report herein the development of organometallic-based discotic liquid crystals. The electronic and luminescent properties of these systems were chosen with an interest in expanding the range of technological applications of liquid crystals in optoelectronic devices, such as light emitting devices,[3] field effect transistors,[4] highly emissive gels,[5] solar cells,[6] and sensors.[7a]

The tendency for a given molecule to display a particular liquid crystal phase is related to its shape, aspect ratio, dipolar properties, conformational dynamics, and specific intermolecular associations. Rod-shaped molecules generally assemble into nematic or smectic phases whereas disc-shaped molecules most often display columnar phases. The projection of a shape need not be in a single molecular subunit and complementary shapes, such as a half disc, can display liquid crystal phases with correlated dynamic organizations of nearest neighbors. In smectic A phases these are referred to as antiphases as a result of the antiparallel correlations of mesogens.[7b] The classic examples are cyanobiphenyl mesogens wherein strong dipolar interactions cause a time-averaged antiparallel organization of nearest neighbors.[8] Similarly in columnar liquid crystals half-disc structures can have anticorrelated structures, and given the larger positional registration between molecules, this type of phase provides opportunities to control the nature and degree of the intermolecular interactions.[9] An attractive feature of columnar phases built up from smaller molecular components is that the mesophase may have a reduced viscosity relative to standard columnar phases based upon discotic mesogens. This latter feature can be advantageous for the assembly of defect free organizations over large distances. The compounds investigated in this study have weaker dipoles than the cyanobiphenyls, but have a strong shape preference for an antiparallel organization. It is important to note that these structures are highly dynamic, and as a result of the liquid nature of the mesophase these correlations extend only for short distances. We anticipate that antiparallel packing in which the bulky flexible chains are, on average, not interacting sterically with those of the nearest neighbors will allow a closer packing of the rigid cores and greater interactions between the metal centers. The resulting molecular alignment could enhance dz^2-orbital overlap in square planar metallomesogens and produce molecular wires that display quasi-one-dimensional conduction.[1]

Organometallic compounds of palladium and platinum based on *ortho*-palladated and *ortho*-platinated nitrogen-substituted aromatic compounds represent an important class of metallomesogens.[10] Most compounds of this type are dinuclear halogen- or carboxylate-bridged metallomesogens combining two rod-like segments. If only one aliphatic chain is attached to the ends of the rod-like segments, the metallomesogens show smectic or nematic phases and larger numbers

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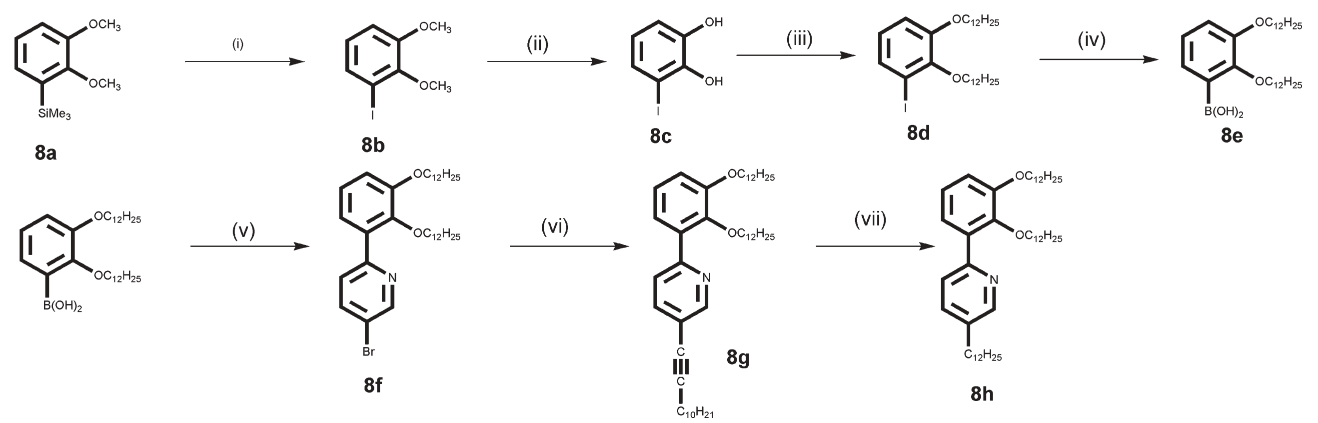


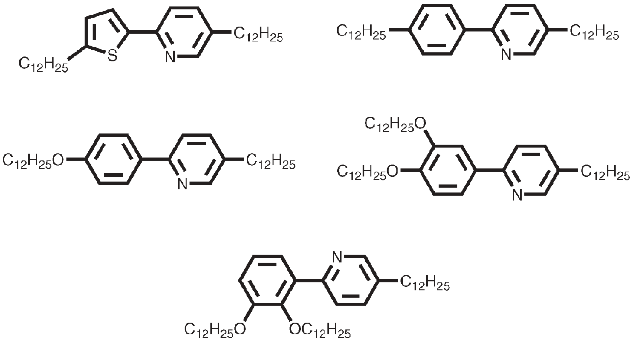
Scheme 1 (i) ICl, CH_2Cl_2, 80%; (ii) BBr_3, CH_2Cl_2, 87%; (iii) $C_{12}H_{25}Br$, K_2CO_3, KI, DMF, 90 °C, 24 h, 61%; (iv) *t*BuLi, $B(OMe)_3$, 63%; (v) 2-iodo-5-bromopyridine, $Pd(PPh_3)_4$, 2 M Na_2CO_3(aq), DME, 86%; (vi) 1-dodecyne, $PdCl_2(PPh_3)_2$, CuI, Et_3N, 57%; (vii) Pd/C, EtOAc, H_2 (45 psi), 52%.

of flexible alkyl chains produce nematic columnar (N_{Col}) and columnar mesophases.[11]

The present study focuses on a series of mononuclear *ortho*-platinated metallomesogens containing a rod-like hetero-aromatic and a half-disc shaped 1,3-diketonate. Previous attempts by other groups to observe mesogenic behavior in related *ortho*-platinated 2-phenylpyridine derivatives have met with limited success.[10] We demonstrate that the number of alkyl or alkoxy chain substitutions on the 2-phenylpyridine and 2-thienylpyridine ligands has a significant effect on the stability of the Col_h phase.

Synthesis

Scheme 1 is representative of the synthetic routes to phenyl pyridine ligands bearing alkoxy groups. Reaction of 3-trimethylsilylveratrol **8a** with ICl in CH_2Cl_2 yields 3-iodoveratrol **8b** in 80% yield. Deprotection of **8b** with BBr_3 yielded 3-iodocatechol **8c** in 87% yield. Heating **8c** in DMF at 90 °C for 24 h with bromododecane in the presence of K_2CO_3 and KI yielded the bisalkylated product **8c** in 61% yield. The corresponding boronic acid was obtained in 63% yield from **8e** by lithium–halogen exchange with *t*BuLi, followed by addition of trimethyl borate and hydrolysis. A Suzuki coupling of **8d** in refluxing DME with 2-iodo-5-bromopyridine in the presence of $Pd(PPh_3)_4$ and 2 M Na_2CO_3 afforded **8f** in 86% yield. Treatment of **8f** with 1-dodecyne in the presence of refluxing Et_3N and $PdCl_2(PPh_3)_2$/CuI gave **8g** in 57% yield and subsequent reduction of **8g** on Pd/C under an atmosphere of H_2 yielded the target ligand **8h** in 52% yield. Other phenylpyridine ligands (Scheme 2) were prepared analogously. The thienylpyridine derivative was synthesized starting from the reaction of 2-thienylmagnesiumbromide with 2,5-dibromopyridine in the presence of Pd(dppb)Cl_2 to afford 2-thienyl-5-bromopyridine in 84% yield. Treatment with Br_2 in CH_2Cl_2 yielded 5-bromo-2-thienyl-5-bromopyridine in 64%. Sonogashira coupling of the dibromo derivative with 1-dodecyne in refluxing Et_3N with $PdCl_2(PPh_3)_2$/CuI and subsequent reduction with Pd/C under an atmosphere of H_2 yielded the target ligand in 95% yield. All synthetic procedures are detailed in the ESI.‡



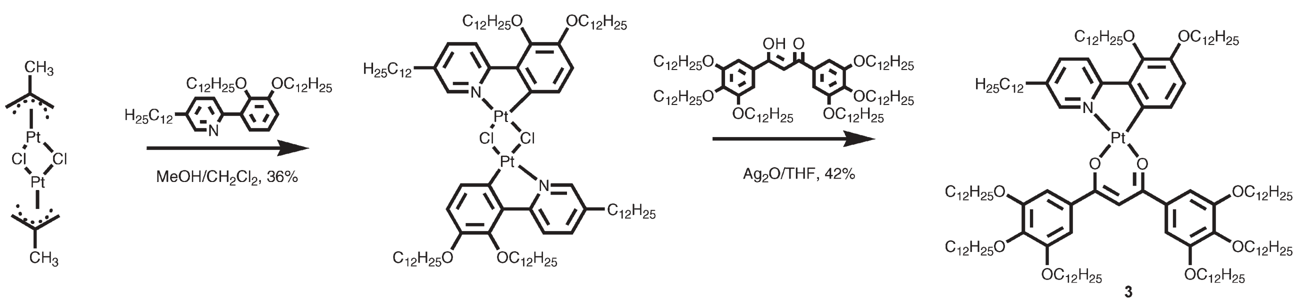
Scheme 2

The dinuclear chloro-bridged complexes were obtained in moderate yields by simply stirring di-μ-chlorobis(η^3-2-methallyl)diplatinum with the corresponding organic ligands (Scheme 3) for 4 days at room temperature in a 1 : 1 mixture of CH_2Cl_2–MeOH.[10] The thienylpyridine derivatives yielded a bis-cyclometalated complex[12] as a side product whose properties are being currently investigated. Reaction with the 1,3-diketonate ligands in THF at 60 °C in the presence of Ag_2O for 24 h afforded the mononuclear *ortho*-metalated complexes. The yield of the final ligand exchange step varied depending upon the cyclometalating ligand. Structures of the complexes synthesized and investigated are shown in Chart 1.

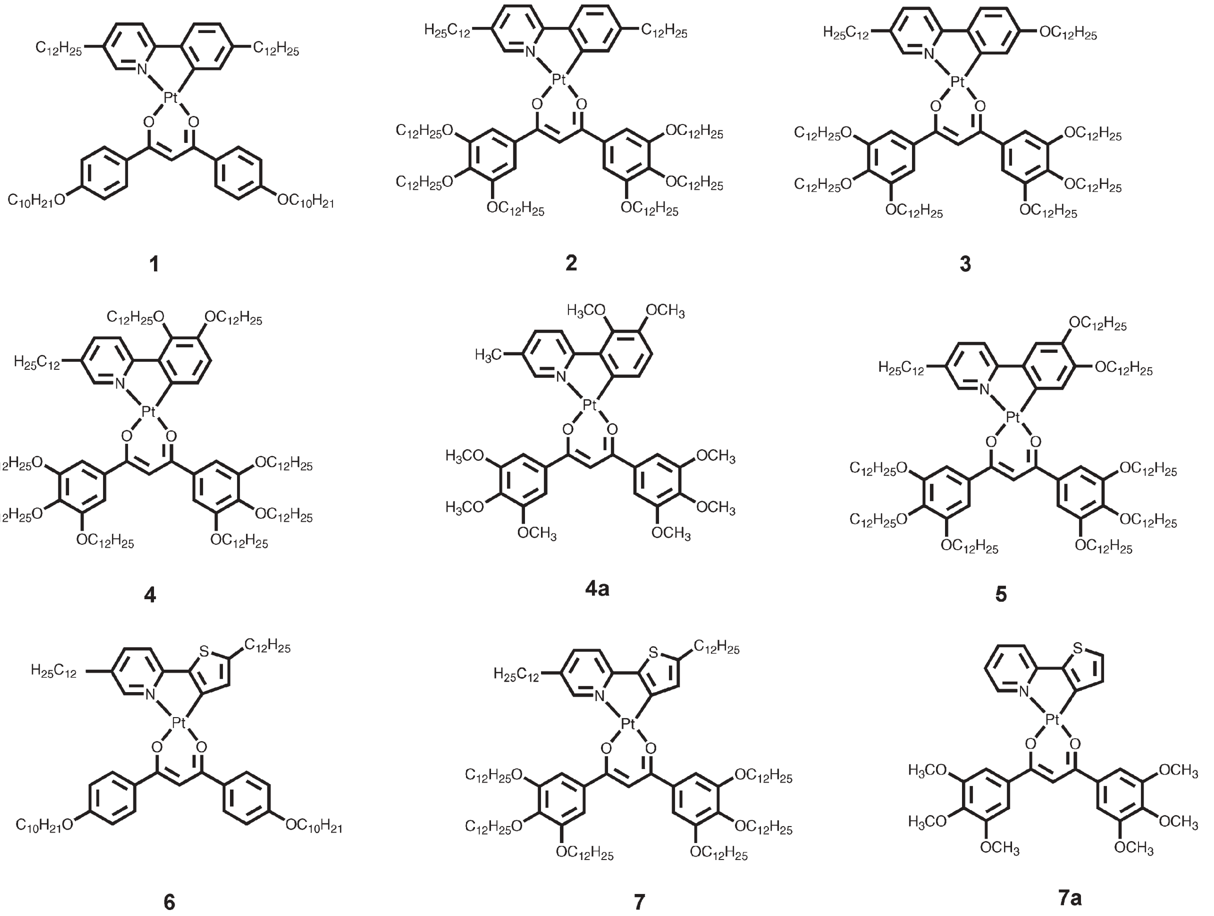
Tschierske and co-workers previously reported[10] that similar *ortho*-platinated compounds were unstable in organic solvents or at elevated temperature. In contrast, we found that all of the compounds reported herein are indefinitely stable in organic solvents and are even stable at high temperatures (200 °C). This revised view of these compounds is important because high stability is a critical issue for any potential applications.

Spectroscopic properties

Highly phosphorescent cyclometalated late-transition metal complexes and materials have been receiving increasing attention for applications in organic-light emitting diodes,[6]



Scheme 3



1 2 3 4 4a 5 6 7 7a

Chart 1

where increased efficiency is achieved by capturing the large percentage of triplet excitons created upon electron–hole recombination. The cyclometalated complexes of iridium(III) and platinum(II) are particularly attractive due to their modular synthesis and high luminescence efficiencies.[13]

Absorption and emission spectra (RT and 77 K) were recorded for all of the complexes and a summary of the data is in Table 1. The energies and the extinction coefficients are similar to those of other cyclometalated Pt complexes reported in the literature.[13c] The solvatochromic transitions in the range of 350–450 nm with extinction coefficients between 2000 and 6000 M^{-1} cm^{-1} are assigned as metal-to-ligand charge

Table 1 Optical properties of Pt(II) complexes[a]

Complex	Absorbance λ_{max}/nm (RT)	Emission λ_{max}/nm RT	Emission λ_{max}/nm 77 K	Φ_p	τ_p/μs
1	353	494	495	0.34	0.5
2	360	533	533	0.30	1.5
3	359	533	522	0.29	1.6
4	359	545	551	0.34	1.5
5	363	520	526	0.32	1.5
6	385	575	570	0.49	11.1
7	385	576	576	0.62	11.3

[a] Room temperature data in toluene. 77 K data in 2-methyl-THF glass

transfer (MLCT) transitions. The higher energy, more intense absorption bands are assigned to π–π* ligand-centered transitions, which are perturbed relative to the free ligand and are not strongly solvatochromic. Metal centered, d–d transitions are not observed for these complexes. It is believed that the strong ligand field of the cyclometalating ligands shifts the d–d transitions to high energy, putting them under the more intense ligand-centered and MLCT transitions.

All of the complexes are intensely emissive in low-temperature glasses (77 K), and most are luminescent in fluid solution (298 K) as well. Most of the complexes also show a small rigidochromic blue shift of 5–10 nm on cooling the sample solution to 77 K. The highly structured emission spectra display vibronic progressions of *ca.* 1400 cm^{-1}, which are typical for breathing modes in aromatic rings. The structured luminescence and microsecond radiative lifetimes at 77 K are consistent with emission originating from a mixed ^{3}ligand-centered-MLCT excited state. Longer lifetimes would be indicative of greater ligand-centered character in the triplet excited state. There is a stark contrast between the emissive quantum yields and lifetimes of the previously reported dipivaloylmethane as compared to the phenyl-substituted β-diketonate ligands in this investigation. Complexes with phenyl-substituted β-diketonate ligands display lower emission efficiencies and excited state lifetimes as low as 35 ns in THF. However, the lifetimes determined at 77 K are about 6–7 μs and similar in magnitude to the dipivaloylmethane-substituted analogues. A reasonable explanation for these observations is the presence of a very weakly or non-emissive diketonate centered excited state that is in thermal equilibrium with the phenylpyridine-centered triplet at room temperature in THF. Indeed, the substitution of aromatic rings on the diketonate ligand extends conjugation and lowers both the oxidation potential and the excited state energy of the ligand. This explanation is also consistent with previously reported fluorine-substituted Pt(II) phenylpyridine complexes having high-energy ligand centered triplet states.[13c] These complexes also display very short lifetimes and low emission quantum yields and equilibration with a non-emissive charge transfer state involving the β-diketonate ligand was also proposed.[14] We also note that phenyl-substituted β-diketonate ligands dramatically reduce the phosphorescence efficiency of cyclometalated Ir(III) complexes in 2-methyl-THF.[13b] We have probed the nature of the very weakly emissive state with a solvent-dependence study. The excited state lifetime changes from approximately 35 ns (THF) to over 2 μs (cyclohexane). In addition, the quantum yield of emission is raised from less than one percent to approximately 25–30%. Therefore, the emission from the lowest energy ^{3}MLCT state remains undisturbed in cyclohexane because the polar CT states are destabilized by the non-polar nature of cyclohexane relative to the more polar THF.[14]

The nature of the cyclometalating ring influences the color of the emission. Complexes with sulfur atoms, which are polarizable and more easily oxidized, have significantly lower transitional energies. Therefore, complexes **6** and **7** display orange-red emissions with a λ_{max} up to 580 nm. Many of these complexes are highly emissive in degassed solutions at RT with lifetimes in the microsecond regime (Table 1).

Table 2 Phase transition temperatures and corresponding enthalpy values

Compound	T/°C (ΔH/kJ mol^{-1})					
1	Cr	146 (21.5)	SmA		156 (5.1)	Iso
2	Cr	80 (47.1)	Col_h		124 (2.4)	Iso
3	Cr	[61 (104.3)	Col_h	73 (11.9)][a]	82 (114.8)	Iso
4	Cr	28 (46.4)	Col_r/Col_h [b]		165 (7.9)	Iso
5	Cr	71 (38.2)	Col_h		159 (6.9)	Iso
6	Cr	110 (39.6)	SmA		123 (4.9)	Iso
7	Cr	73 (28.4)	Col_h		117 (2.4)	Iso

[a] Monotropic phase transition. [b] Temperature dependent X-ray diffraction measurements (cooling run) showed a change in the lattice from a Col_h to the Col_r phase between 80 °C and 90 °C, however, the exact transition temperature could not be retrieved by DSC or optical microscopy.

Liquid crystalline properties

The mesomorphic properties of the obtained compounds were investigated using polarized optical microscopy (POM), differential scanning calorimetry (DSC) and powder X-ray diffraction (XRD). The transition temperatures, corresponding enthalpy values, and mesophase types observed for the series of platinum complexes are summarized in Table 2.

Polarized light optical microscopy

The compounds with four alkyl chains, **1** and **6**, exhibit an enantiotropic smectic A phase (Fig. 1), displaying a characteristic fan-shaped optical defect texture in combination with black homeotropic areas. The corresponding compounds with 6 aliphatic tails (using the 3,3′,4,4′-tetradodecylphenyl-diketonate, which is not shown here) did not display mesomorphic behavior. A further increase in the number of tails to eight (compounds **2**, **3**, **4**, **5** and **7**) results in the formation of columnar mesophases, which were characterized by typical spherulitic textures accompanied by dark homeotropically ordered regions.

Compounds **2** and **3** differ only by a single oxygen atom connecting the flexible tails. The melting temperatures of the two compounds are very similar, however, the columnar phase of **2** is strongly stabilized compared to **3**, which displays only a monotropic mesophase. The lower clearing temperature of **3** contrasts with the usual observation that alkoxy chains generally lead to higher clearing temperatures than the alkyl counterparts. To further examine structure–property correlations we investigated metallomesogens containing phenylpyridine ligands with dodecyloxy tails, varying in number and position (**3**–**5**). Compounds **4** and **5** bear the same number of alkoxy chains on the phenylpyridine. The observed clearing temperatures are of the same order, but they display a significant difference in the melting temperatures. A possible explanation for this is that **4**, due to steric interactions, is non-planar in the liquid (crystalline) phase. This induces the formation of a racemic mixture of stereoisomers that is harder to pack sterically and thus exhibits a lower crystallization temperature. As a result, compound **4** exhibits a wide liquid crystalline phase possessing a mesophase near room temperature. Compounds **2** and **7** have the same melting and clearing temperatures in spite of a significant difference in the

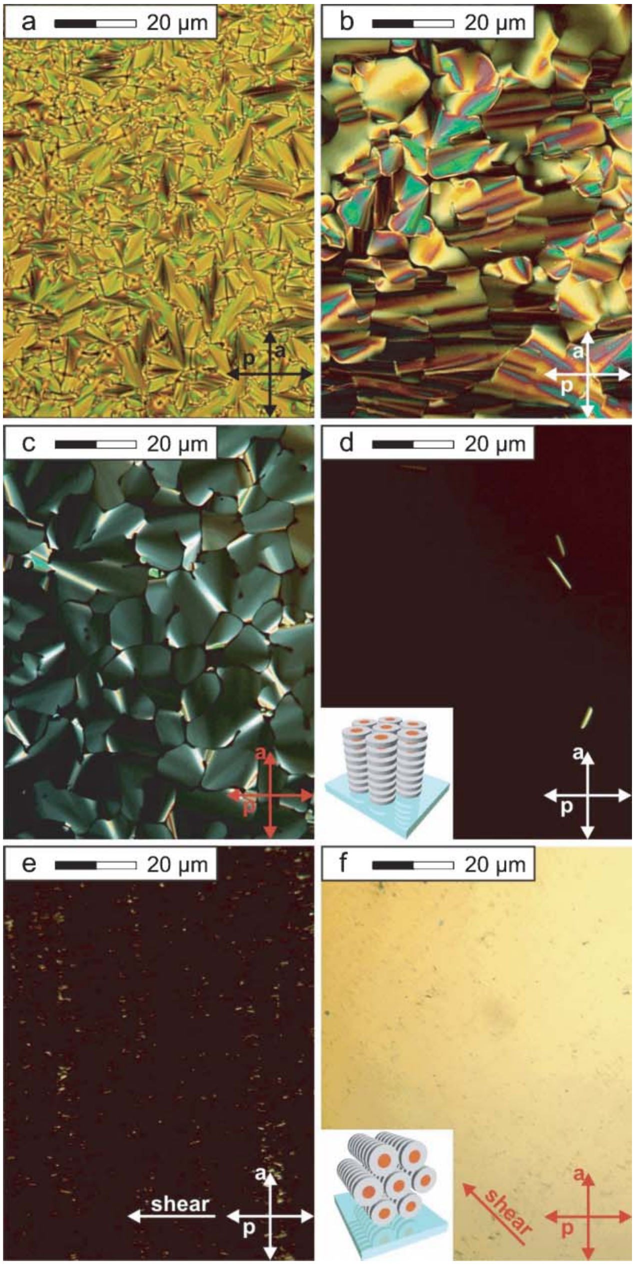


Fig. 1 Optical polarizing microscopy pictures of: (a) **6** at 118 °C (SmA phase); (b) **4** at 120 °C (Col$_h$ phase). Both samples sandwiched between unfunctionalized glass slides. Aligned samples of **4** at 85 °C (Col$_h$ phase) between glass slides functionalized with 3-aminopropyltriethoxysilane: (c) upon cooling from the isotropic phase (no annealing); (d) after annealing overnight at 160 °C (homeotropic alignment); (e,f) after shearing the homeotropic sample: rotation of the stage gives minima and maxima in the birefringence (shearing direction indicated). All pictures taken between a crossed polarizer and analyzer; the scale bar indicates the magnification.

cyclometalating ligand, with the former bearing a phenylpyridine ligand and the latter a thienylpyridine ligand.

Macroscopic alignment of liquid crystal systems is crucial for applications, but is usually hard to realize with viscous metallomesogenic columnar phases. We tested two surface treatments to yield macroscopically aligned structures. Glass slides and ITO covered glass slides were treated with hexadecyltriethoxysilane (hydrophobic) or 3-aminopropyltriethoxysilane (hydrophilic). Our samples were placed between the functionalized slides, heated into the isotropic phase and then cooled to 5 °C below the phase transition temperature. For hydrophobic substrates the domains did not merge after prolonged annealing. In contrast, hydrophilic substrates showed near perfect homeotropic alignment after annealing overnight (Fig. 1d). We speculate that the favorable interaction of the amino group with the platinum core plays a key role in the alignment process.[15] Shearing of the latter samples at elevated temperatures gave a well-oriented homogeneous columnar phase (Fig. 1e,f), which remained stable after continued annealing.

Powder X-ray diffraction

Selected mesogens were subjected to temperature dependent powder X-ray diffraction (XRD) measurements. The results are summarized in Table 3.

The X-ray diffraction pattern in the Col$_h$ phases shows a strong fundamental reflection at spacing d_{100}, followed by a series of small, but sharp small angle reflections at spacings $d/\sqrt{3}$, $d/\sqrt{4}$, $d/\sqrt{7}$ (Fig. 2a), characteristic of a hexagonal packing. Mesogens **2** and **4** show lattice constants a (and columnar

Table 3 Powder X-ray diffraction data

Compound	T/°C	Phase and symmetry	Miller indices	$d_{hkl,\mathrm{exp}}$/ Å	$d_{hkl,\mathrm{calc}}$/ Å	Lattice constants[a]
2	90	Col$_h$	100	26.1	26.2	a = 30.2 Å
		p6mm	110	15.2	15.1	γ = 60°
			200	13.1	13.1	S_{XRD} = 0.79 nm^2
			alkyl (diffuse)	4.4	—	
			001	3.7 [b]	—	
3	70	Col$_h$	100	30.9	31.0	a = 35.8 Å
		p6mm	110	17.9	17.9	γ = 60°
			200	15.6	15.5	S_{XRD} = 1.11 nm^2
			210	11.8	11.7	
			alkyl (diffuse)	4.4	—	
			001	3.7 [b]	—	
4	120	Col$_h$	100	25.4	25.4	a = 29.4 Å
		p6mm	110	14.7	14.7	γ = 60°
			200	12.7	12.7	S_{XRD} = 0.75 nm^2
			alkyl (diffuse)	4.3	—	
			001	—	—	
	50	Col$_r$	110	25.9	25.8	a = 48.9 Å
		c2mm [c]	200	24.5	24.4	b = 30.5 Å
			020	15.2	15.3	γ = 90°
			310	14.4	14.5	S_{XRD} = 0.75 nm^2
			220	12.9	13.0	
			400	12.2	12.4	
			alkyl (diffuse)	4.4	—	
			001	3.67	—	

[a] The *p6mm* Col$_h$ lattice parameter $a = 2\langle d_{100}\rangle/\sqrt{3}$, with $\langle d_{100}\rangle = [d_{100} + (\sqrt{3})d_{110} + (\sqrt{4})d_{200}]/3$. The columnar surface area in the Col$_h$ phase: $S_{\mathrm{XRD}} = (\sqrt{3})a^2/2$; in the Col$_r$ phase: $S_{\mathrm{XRD}} = ab/2$, considering that in this phase two molecules form a unit cell. [b] Weak reflection. [c] Lattice parameters a and b were determined by fitting the experimental reflections to a *c2mm* lattice.

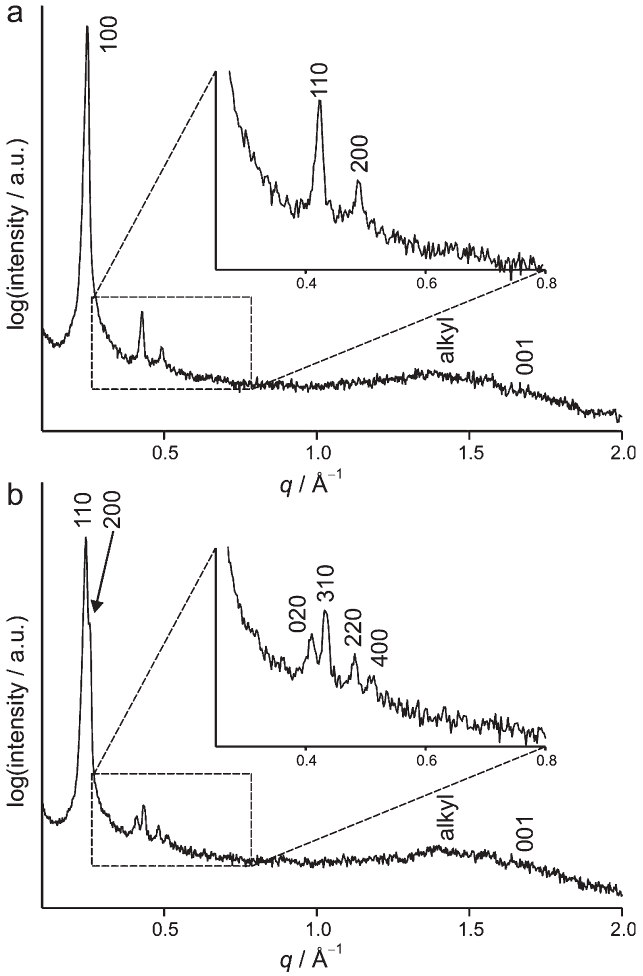


Fig. 2 Powder X-ray diffractograms of **4** at (a) 120 °C (Col$_h$ phase) and (b) 50 °C (Col$_r$ phase).

surface areas *S*) that are nearly identical (∼30 Å). This value is slightly larger than values observed earlier for antiparallel-organised columnar phases of mesogens of the same diketonate ligand and lacking a second organic ligand,[9a] suggesting the formation of a locally antiparallel structure for **2** and **4**. The lattice constant of **3** is substantially larger, indicating a different packing of the mesogens inside the columnar structure. Our XRD results, however, are not conclusive on this point, due the intra-columnar disorder manifested by the weak or absent (001) reflections, and more experimental effort is needed for an exact determination of the molecular packing inside the columns.

Mesogen **4** shows a rectangular columnar phase at lower temperatures, indicated by a doubling of the number of reflections at small angles (Fig. 2b). The experimental small angle X-ray data could be fit satisfactorily to a rectangular *c2mm* lattice,[16] which is a columnar phase with all of the discotic mesogens aligned (or tilted) in the same direction. The Col$_h$–Col$_r$ phase transition could not be observed in POM or DSC experiments, which may not come as a surprise considering the small changes in the 2D columnar lattice. The X-ray crystal structure of **4** shows a close antiparallel stacking and hence the transition to Col$_r$ may reflect a higher antiparallel correlation and hence a tendency to lower symmetry. Although the crystal structure shows a fairly flat structure in the solid state, calculations by Tschierske and co-workers[10c] show that the non-planar phenylpyridine rings could arise from the C–H interaction between the adjacent rings. The phenylpyridine is twisted in the liquid (crystalline) phase, but not in the crystal phase, likely causing disorder in the columnar direction, causing the weak (001) reflections, and hence we do not observe a broad reflection at about 7 Å which has previously been assigned to a doubling of the periodic structure along the column in systems with strong antiparallel correlations.[9]

Single crystal X-ray diffraction

To gain insight into the organizational preferences of the mesogenic core, model compounds **4a** and **7a** were synthesized and their solid-state structure was established by a single crystal X-ray diffraction study (Fig. 3). In **4a**, the molecules

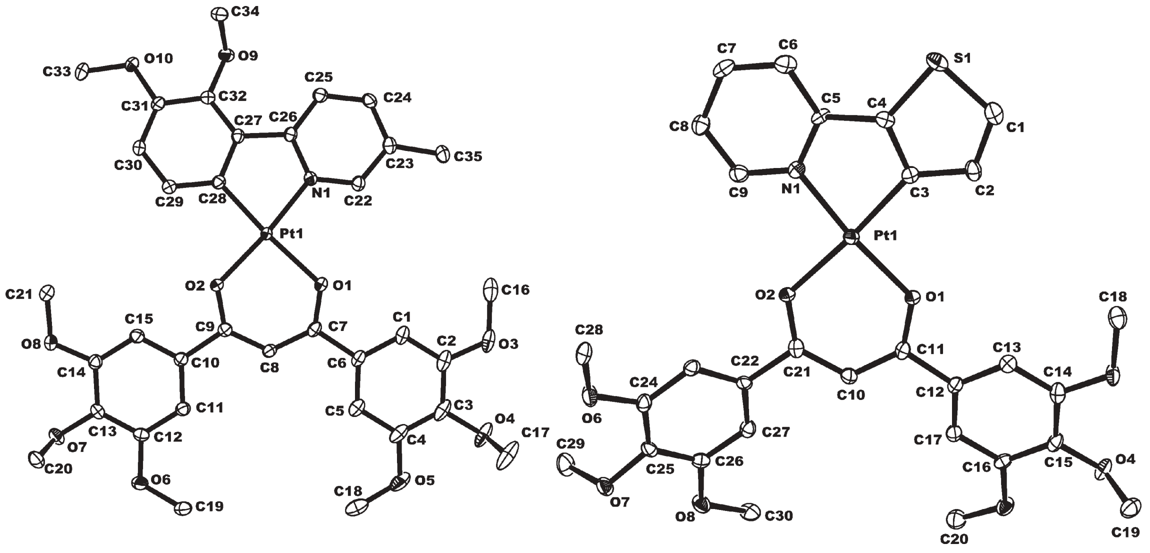


Fig. 3 Thermal ellipsoid plots of **4a** (left) and **7a** (right) at 50% probability. Hydrogen atoms, disordered atoms and solvent molecules are omitted for clarity.

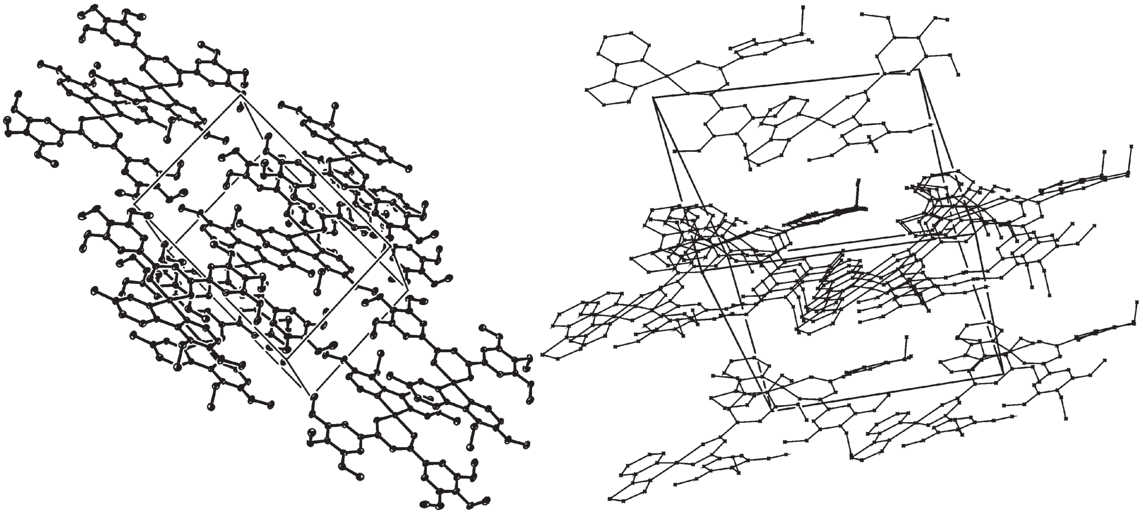


Fig. 4 Crystal packing of compounds **4a** (left) and **7a** (right) showing antiparallel and parallel stacking of two molecules respectively.

exhibit a packing arrangement in the expected antiparallel fashion with a Pt–Pt distance of 4.6878(10) Å (Fig. 4). In contrast, **7a** shows a parallel arrangement and a long Pt–Pt distance of 8.422(7) Å. This shows the ability of ligand substitution to influence packing arrangement and Pt–Pt distances.

Conclusion

New mononuclear *ortho*-platinated metallomesogens have been synthesized. By increasing the number of alkyl chains attached to the cyclometalating ligand and the 1,3-diketonate units, a transition from lamellar to columnar organization was observed. We find that the distribution of the flexible sidechains around the cyclometalating ligand has a dramatic effect on the mesophase stabilization. Solid state structures determined by single crystal X-ray diffraction studies show a significant difference in the arrangement of the molecules between the phenylpyridine and thienylpyridine derivatives. The excited state properties of these molecules are altered depending on the cyclometalating ligand in these molecules.

Acknowledgements

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