JOURNAL OF
Materials
CHEMISTRY
Communication

Calamitic smectic liquid crystalline supramolecular architecture from octaalkoxy-substituted Pd^{II}–η^1-benzylideneaniline complexes

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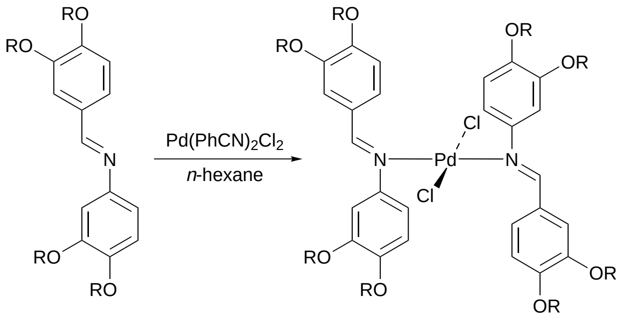
Octaalkoxy substituted Pd^{II}–η^1-benzylideneaniline complexes with a more disc-like shape can give rise to a calamitic smectic phase and low melting transition temperatures comparable to those of the corresponding free ligands.

It is well documented that in general the number of peripheral aliphatic chains connected to an aromatic core and the anisotropic shape in metallomesogens are main factors in determining their supramolecular structure in the liquid crystalline phase.[1–7] Lamellar arrangements of liquid crystalline phases are formed for molecules with two to four peripheral chains, whereas columnar arrangements are exhibited by metallomesogens with six or more flexible aliphatic chains peripherally connected to a central aromatic core. For example, dinuclear orthopalladated imine complexes with tetrasubstituted aliphatic chains are reported to show calamitic smectic phases.[8] On the other hand, the presence of four additional chains in the aromatic core of dinuclear orthopalladated complexes produces a more disc-like molecular shape, thus leading to the formation of the discotic mesophase.[9] This can be explained by the fact that the main factor governing the geometry of supramolecular structure in the liquid crystalline phase is the ratio of the volume occupied by the rigid core to the volume filled by the flexible peripheral substituents of the molecules.

Here we report on the first examples of more disc-like octaalkoxy-substituted mononuclear Pd^{II} metallomesogens with η^1-benzylideneaniline giving rise to a calamitic smectic A mesophase and low melting transition temperatures comparable to those of the corresponding free ligands in contrast to those of palladium(II) orthometallated complexes.[8] The mononuclear palladium complexes with monodentate imine ligands without orthocyclopalladation were synthesized by a ligand exchange reaction with [Pd(PhCN)$_2$Cl$_2$] and the corresponding imine ligands as shown in Scheme 1. The complexes were purified by column chromatography (silica gel) using methylene chloride as eluent, and were obtained in 44–53% yields. Satisfactory analytical data were obtained for all the compounds.† Also, an X-ray crystallographic analysis performed for a model compound[10] has confirmed that the molecular structure appeared to be the Pd^{II} complex with η^1-benylideneaniline. The mesomorphic properties of imine ligands **1**, **2** and the complexes **3**, **4** were studied using differential scanning calorimetry (DSC) and thermal optical polarized microscopy. Fig. 1 presents the DSC traces for the complexes obtained from the cooling scans. The thermal properties of the complexes are summarized and compared with those of the corresponding ligands in Table 1.



R = CH$_3$(CH$_2$)$_5$ **1**
CH$_3$(CH$_2$)$_9$ **2**

R = CH$_3$(CH$_2$)$_5$ **3**
CH$_3$(CH$_2$)$_9$ **4**

Scheme 1 Synthesis of Pd^{II} complexes with η^1-benzylideneaniline

Both imine ligands exhibit only a crystalline melting and do not show liquid crystalline phase behavior. In contrast to the thermal behavior of the ligands, the palladium complexes exhibit a liquid crystalline phase. Complex **3** with hexyloxy peripheral chains melts into an isotropic liquid at 91.8 °C. On cooling from the isotropic liquid, first batônnet-like growth of texture can be observed with a final development of focal conic domains which are characteristic of a smectic A mesophase exhibited by conventional calamitic mesogens. Thus, the

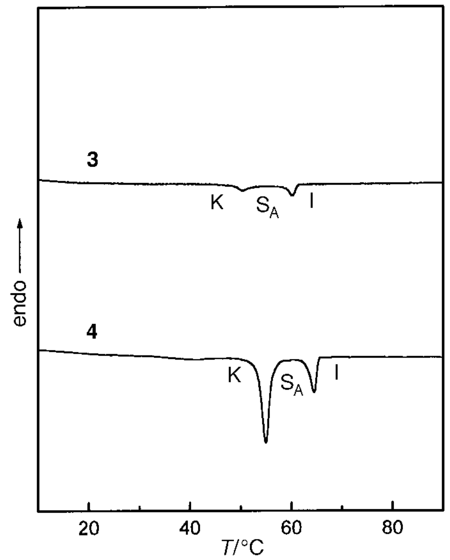


Fig. 1 DSC traces (10 °C min^{-1}) recorded during the first cooling scans of **3** and **4**

Table 1 Thermal transitions of the imine ligands and the Pd complexes (K, crystalline phase, S_A, smectic A phase, I, isotropic phase)

	phase transitions/°C and corresponding enthalpy changes/kJ mol^{-1}	
compound	heating	cooling
1	K 84.2 (45.2) I	I 71.0 (44.6) K
2	K 95.5 (90.1) I	I 74.4 (90.7) K
3	K 91.8 (24.5) I	I 61.2 (1.5) S_A 50.3 (0.9) K
4	K 79.7 (19.3) I	I 64.5 (4.3) S_A 55.0 (13.2) K

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† Supplementary material (SUP. **57325**, 4 pp.) available from the British Library. Details are available from the editorial office.

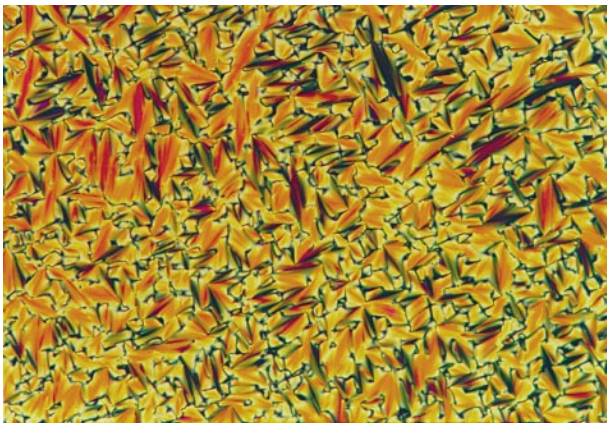

Fig. 2 Representative optical polarized micrograph (100×) of the texture exhibited by the smectic A mesophase of **4** at 64 °C on the cooling scan

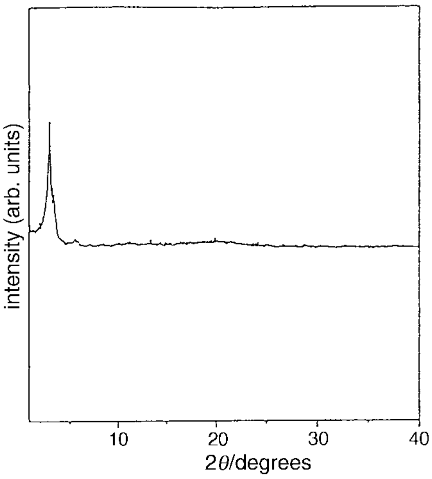

Fig. 3 Wide angle X-ray diffraction pattern for compound **4** at 60 °C on cooling

smectic A liquid crystalline phase of **3** is monotropic. Complex **4** with decyloxy peripheral chains shows similar thermal behavior to **3** which exhibits a monotropic smectic A mesophase. On heating, **4** melts into an isotropic liquid at 79.7 °C which is an even lower melting transition temperature than that of the corresponding ligand. The transition from the isotropic liquid can be seen by the formation of a focal conic fan-like texture indicating a smectic A mesophase as shown in Fig. 2.[11] Induction of comparable or even lower melting transition temperatures in the complexes compared to those of the ligands is very rare in calamitic metallomesogenic systems, and is rewarding with respect to their potential processability. This is mainly due to disturbance of the crystal packing of the molecules caused by the chlorine atoms which are out of the plane of the aromatic core.

Preliminary X-ray diffraction measurements have been performed on the mesophase of complex **4**. The X-ray pattern of **4** exhibits two Bragg reflections in the small angle region with the ratio of positions of 1:2 and a diffuse scattering in the wide angle region as shown in Fig. 3. This result supports the existence of a disordered smectic mesophase. The existence of a layered smectic phase is in contrast with the normal behavior of disc-like octasubstituted metallomesogens which show a columnar type of supramolecular structure. The aromatic moieties of the imine ligands attached to a central metal will be twisted out of coplanar geometry to reduce steric repulsion. This distortion may provide a larger space for chains, and thus the peripheral chains are still not able to fill the space around the core efficiently. Consequently, the flexible chains tend to align in a preferred direction, leading to the lamellar self organization. This explains qualitatively the phase behavior of this palladium complex system.

Financial support of this work by the Non Directed Research Fund, the Korea Research Foundation (1996) is gratefully acknowledged. We also acknowledge Mr. J. H. Im for the synthesis of a model compound and Prof. W.-C. Zin for X-ray powder diffraction experiments.

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10 We have synthesized bis[η^1(N)-4-ethyloxybenzylidene-4′-ethyloxyaniline]dichloropalladium(II) as a model compound in order to confirm the molecular structure by a single crystal X-ray structural analysis. Full crystallographic details, excluding structure factors have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/75.
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Communication 7/08128F; *Received* 11*th November*, 1997