

Supramolecular metallomesogens. Self-organization of an H-bonded tetrameric assembly into columnar phase from single component†

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The first example of supramolecular metallomesogens derived from palladium complexes exhibiting columnar phase is reported, and the formation of the mesophase is induced by H-bonding in a tetrameric assembly.

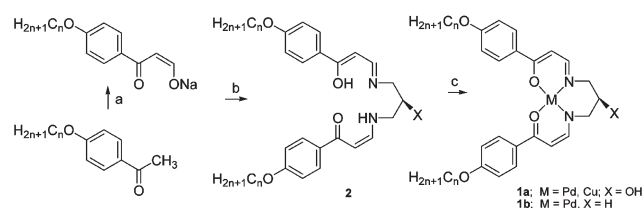
The definition of supramolecular chemistry was well clarified in the very first words of Lehn's Nobel lecture: "The chemistry of the intermolecular bond, covering the structures and functions of the entities formed by association of two or more chemical species." According to the point of view, liquid crystals formed by intermolecular stacking give the macro-orientations spontaneously and inspire scientists to realize new mesogens toward specialized supramolecules.¹ In the improvements of molecular electronics, the manner *via* liquid crystals opposite to "top-down" process, such as vapor deposition, *etc.* is one of the chemical approaches for materials with the "bottom-up" nature.² On the other hand, molecular architecture, which dominates the process of self-assembly, can be applied to achieve advanced nanostructures.³ Polyphilic mesogens were applied to complex morphologies,⁴ liquid crystals performed a strong amplification of the optical response were formed by covalent donor-acceptor complexes,⁵ and chiral architectures were also revealed by helical mesophases.⁶ Furthermore, tubular mesophases with macrocyclic receptors can lead to ion channels.⁷

The research in supramolecular H-bonding liquid crystals has been studied extensively during the past decades, and the subject was also reviewed.⁸ Liquid crystals derived from complementary components through single or multiple H-bonding can be formed. Anisotropic phases provided by non-mesogenic H-donors and H-acceptors are influenced by dynamic characters of H-bonds, and differ from conventional liquid crystalline π - π interactions.⁹ A variety of novel structural types were modeled^{8,10} and many examples were proposed.¹¹ Metal incorporated liquid crystals, so-called metallomesogens, attract considerable attention in LC materials. Interesting physical and chemical properties are manipulated by the electronic states of contained metals.¹² A novel chelate derived from 8-quinolinolato platinum(II)^{12c} was used to generate phosphorescent organogel materials. This

approach in synthetic strategy is now continued and reveals more and more novel constructions.¹³

Numerous metallomesogens exhibiting columnar phases have been reported.¹³ Some of them were constructed with half-disc molecules, and their mesomorphic properties were found to be sensitive to the structure of the bridging moiety. However, examples of metallomesogens¹⁴ formed or induced by H-bonding interaction still remain unknown. In this work we describe the generation of supramolecular liquid crystals by palladium complexes **1** (Scheme 1) in which H-bonded metallomesogens emerged from a single component. This is, to our best knowledge, the first example appended with only two sidechains exhibiting a columnar phase, and the formation of the columnar phase is induced by an H-bonded supramolecular tetramer. Most compounds with only two side chains are not expected to give any columnar phase since they do not fill space very efficiently. However, a few examples^{15,16} of metallomesogens with three side chains, which exhibited columnar phases have been reported. An antiparallel arrangement within the columns has generally been proposed in this type of correlated columnar phase.

The compounds were prepared according to Scheme 1. The light yellow solid Schiff bases were obtained by the reaction of the freshly prepared sodium salts with 1,3-diamino-2-propanol. The reaction of the Schiff bases with Pd(OAc)₂ or Cu(OAc)₂ gave the metal complexes.‡ The crystal and molecular structure of Pd complex **1a** ($n = 3$) was determined by means of X-ray structural analysis,¹⁷ with the ORTEP plot shown in Fig. 1. The geometry at the palladium center is slightly twisted square planar, and the Pd(II) atom essentially sits in the central plane defined by the four coordinating atoms N1, O1, Pd, N2 and O3. The phase temperatures and enthalpies of compounds **1** are listed in Table 1. All palladium complexes **1a** with longer chains ($n = 14, 16, 18$) were truly mesogenic, however, other palladium complexes ($n = 10, 12$) and the copper complex **1a** ($n = 16$) were in fact non-mesogenic.



Scheme 1 Reagents and conditions: (a) Na, Et₂O, HCOOEt, stirring at rt for 24 h; 54–61%; (b) 2-hydroxy-1,3-propanediamine (0.55 eq.), acetic acid (3 drops), reflux in CH₂Cl₂ for 24 h; 71–76%; (c) M(OAc)₂ (M = Pd or Cu; 1.1 eq.), reflux in THF–EtOH for 4 h; 85–92%.

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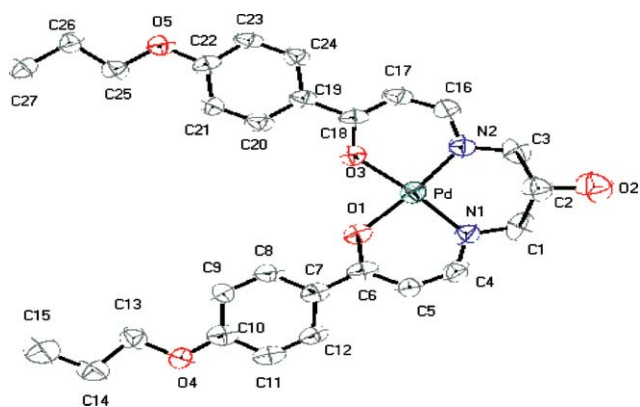


Fig. 1 ORTEP of Pd complex **1a** ($n = 3$) with atom-numbering scheme and at 50% probability level. A two-site disorder was found with equatorial C2'O2 (0.55 occupancy) and axial C2'O2' (0.45 occupancy).

Table 1 Phase behavior of metal complexes **1a** and **1b**

1a (Pd, $n = 10$)	$\text{Cr}_1 \xrightarrow[146.9(2.54)]{149.2(2.73)} \text{Cr}_2 \xrightarrow[168.6(29.5)]{173.9(29.7)} \text{I}$
1a (Pd, $n = 12$)	$\text{Cr}_1 \xrightarrow[145.1(1.92)]{147.1(1.93)} \text{Cr}_2 \xrightarrow[171.2(31.1)]{174.8(31.3)} \text{I}$
1a (Pd, $n = 14$)	$\text{Cr}_1 \xrightarrow[65.6(14.6)]{65.8(15.5)} \text{Cr}_2 \xrightarrow[117.3(0.13)]{119.3(0.22)} \text{Col}_h \xrightarrow[169.9(29.4)]{177.8(30.0)} \text{I}$
1a (Pd, $n = 16$)	$\text{Cr}_1 \xrightarrow[44.2(13.7)]{47.0(13.4)} \text{Cr}_2 \xrightarrow[168.2(15.2)]{100.9(1.64)} \text{Col}_h \xrightarrow[172.6(16.9)]{172.6(16.9)} \text{I}$
1a (Pd, $n = 18$)	$\text{Cr}_1 \xrightarrow[32.7(13.2)]{40.5(14.7)} \text{Col}_h \xrightarrow[164.4(10.5)]{169.6(11.4)} \text{I}$
1a (Cu, $n = 16$)	$\text{Cr} \xrightarrow[94.3(27.4)]{117.1(26.7)} \text{I}$
1b (Pd, $n = 16$)	$\text{Cr}_1 \xrightarrow[61.8(17.3)]{65.2(17.6)} \text{Cr}_2 \xrightarrow[94.8(67.1)]{119.7(67.2)} \text{I}$

The electronic configuration (Pd^{2+}/d^8 , Cu^{2+}/d^9) and/or central geometry (Pd^{2+}/SP , $\text{Cu}^{2+}/\text{T}_d$) have played an important key in forming such novel structure and mesogenic behavior. These complexes gave two typical transitions of crystal-to-columnar and columnar-to-isotropic ($\text{Cr} \rightarrow \text{Col} \rightarrow \text{I}$), observed in most discotic molecules reported. The clearing temperatures were in the range 169.6–177.8 °C, and the temperature range of the mesophase increased with increasing length of the alkoxy chains. The mesophase was characteristically identified as a columnar phase under an optical microscope. We observed two textures (Fig. 2(a)): pseudo-focal-conics and also a blade-like region. A powder X-ray diffraction experiment confirmed the columnar phases. A typical pattern of one stronger and two weaker peaks at lower angle and one diffuse broad peak at wide angle were observed with a spacing ratio of $1 : (1/3)^{1/2} : (1/7)^{1/2}$. The diffraction pattern (Fig. 2(b))

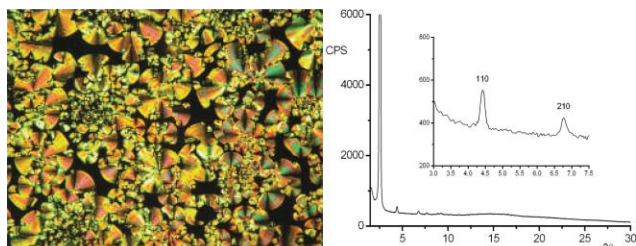


Fig. 2 Optical texture of Col_h of compound **1a** (Pd, $n = 18$) at 60 °C, and powder XRD plot of compound **1a** (Pd, $n = 16$) at 165 °C.

corresponded to a Col_h columnar arrangement, corresponding to (10), (11) and (21), giving a lattice constant of 35.44 Å ($n = 16$). This value is quite close to the theoretical value (for example, 32.84 Å for $n = 16$) obtained from single-crystal data, supporting the proposed tetrameric structure in the mesophase.

The overall molecular shape of monomeric palladium compound is in fact considered as triangular based on the angle 56.0°, defined by C7, C2 and C19 atoms measured from single-crystal data. Most of stable discotic mesogens contain six to eight sidechains. The formation of a Col_h phase in this system was attributed to the H-bonding interaction generated by a tetrameric structure, shown in Fig. 3. The hydroxyl groups at bridging C₂ are guided directly to a central focal point, four molecules linked together by H-bondings to each other. On the other side of the molecules, the alkyl chains whose orientations are maintained by the four palladium complexes radiate far and near/wide. A perfectly supramolecular discotic tetrameric structure with eight side chains in total is formed, which led to the final configuration needed for columnar mesomorphism. In order to assert the formation of the columnar phase by H-bonding, rather than by general shape complementarity, a similar Pd complex **1b** ($n = 16$) was also prepared and studied. However, only a transition $\text{Cr} \rightarrow \text{I}$ was observed.

Two key steps are crucial in constructing this unique macro-tetramer; the palladium coordination and hydrogen bonding as driving forces in forming the columnar phase. The palladium coordination determined by the chemical structure keeps all sidechains away from interacting with each other, and the hydrogen bonding facilitates the original triangular molecule showing a new morphology of an overall discotic shape. Herein, an appropriate aspect ratio is achieved to satisfy the column packing. The four molecules within a column in the tetramer do not possess the same plane but rather an awl shape, and the columns in the hexagonal phase are not directly aligned but rather alternate. The alternating alignment shown in the unit cell packing indicates necessary intercalation or the tendency of self-assembly might facilitate hexagonal columnar formation.

In conclusion, a new type of unique H-bonded supramolecular metallomesogenic complexes exhibiting columnar phases was

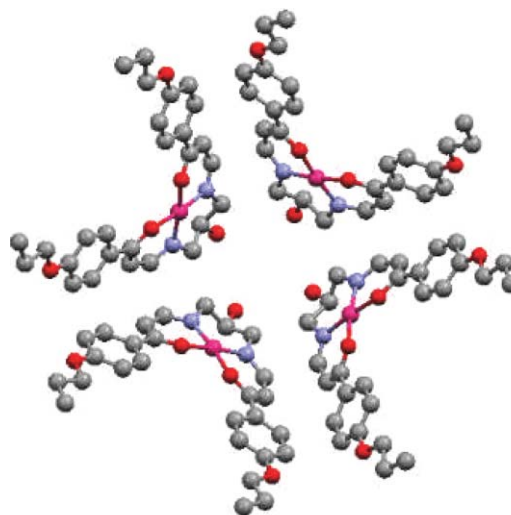


Fig. 3 A supramolecular tetrameric structure formed by H-bondings.

prepared. This is the first example with only two sidechains, in which the mesophase was induced by a H-bonded tetrameric superstructure from a single component.

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Notes and references

‡ **Palladium complex 1a** ($n = 14$): a solution of *N,N'*-bis[1-(4'-tetradecyloxyphenyl)-3-oxopropenyl]-2-hydroxypropylenediamine (0.20 g) dissolved in 5.0 mL of CH_2Cl_2 was added a solution of palladium acetate (58.0 mg) in CH_3OH (2.0 mL). The solution was refluxed for 4 h and then concentrated to dryness, and 10 mL CH_2Cl_2 was added. The solution was then filtered and concentrated to give yellow solids. The residue was purified by column chromatography (silica gel, CH_2Cl_2). Yellow solids were obtained after recrystallization from CH_2Cl_2 - CH_3OH . Yield 78%. Anal. Calc. for $\text{C}_{49}\text{H}_{76}\text{N}_2\text{O}_5\text{Pd}$: C, 66.91; H, 8.71; N, 3.18. Found: C, 66.65; H, 8.30; N, 3.07%.

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- X-Ray crystallographic data for **1a** (Pd, $n = 3$): $\text{C}_{27}\text{H}_{32}\text{N}_2\text{O}_5\text{Pd}$, $M = 570.95$, tetragonal, space group $P4_2/n$, $a = 26.5422(11)$, $b = 26.5422(11)$, $c = 7.1719(3)$ Å, $V = 5052.5(4)$ Å³, $Z = 8$, $T = 150$ K, $D_c = 1.501$ g cm⁻³, 14711 reflections measured, 5702 unique which were used in all calculations. $R_1 = 0.0477$ ($I > 2.0\sigma(I)$), $wR_2 = 0.1268$ (observed data). CCDC 619245. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612374k.