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A robust Ti(IV)-based mesogen constructed around a TiO₄N₂ core

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The stable complexes [Ti(1a)(2)₂] and [Ti(1b)(2)₂], where **2** is the 6,6'-diphenyl-2,2'-biphenolato ligand and the **1a** and **1b** ligands are 2,2'-bipyrimidine derivatives, are synthesized. The complex [Ti(1b)(2)₂] containing a diimine ligand substituted with long alkyl chains (C₁₆) exhibits an original liquid crystal behaviour. This property and the self-assembling in the crystalline state are explained by the particular molecular conformation of the complexes.

The mesomorphic or liquid-crystalline state combining both order and mobility is well known to promote unique properties and applications ranging from display technology through templating media for synthesis to biological activity (targeting and drugs transportation and gene materials).¹ For thermotropic liquid crystals the supramolecular organisation as temperature function is governed by the proportion of two rigid / flexible antagonistic parts also called amphipathic character. A particular class of mesogenic species are metallomesogens,² which are metal complexes that exhibit liquid-crystalline properties; they have become the target of intensive research over the past decades because of the properties arising from the presence of metal ions. Thus, mesogens incorporating various metals such as copper, silver, gold, vanadium, iron, zinc, mercury, nickel, palladium, platinum, iridium, have been developed.³

Titanium (IV) complexes represent a major class of compounds widely used in many fields of modern molecular science. Organometallic and coordination titanium (IV) compounds are powerful reagents for catalytic enantioselective processes,⁴ for catalytic organic transformations, as initiators for polymerisation reactions,⁵ or for biological and medical applications.⁶ Also, Titanium-based materials (TiO₂ or hybrid materials) occupies a central place in material sciences.⁷ Therefore, we were intrigued by the fact that Ti(IV)-based mesogens have not been reported so far.⁸ We attribute this lack of reports to the moderate stability usually displayed by Ti(IV) complexes rendering difficult the study of the potential mesogenic properties.

Over the latest decade, we have synthesised a series of well-defined mononuclear titanium(IV) complexes constructed around a TiO₄N₂ framework⁹ using the 6,6'-diphenyl-2,2'-biphenol proligand (**2-H₂**, Chart 1).¹⁰ Interestingly, this family of complexes shows a good hydrolytic stability, in particular when substituted 2,2'-bipyrimidine ligands are incorporated in these architectures.¹¹

Chart 1

We report herein the synthesis of robust titanium complexes where the diimine ligands are the 2,2'-bipyrimidine derivatives **1a** and **1b**. Compound **1a** incorporates a 3,4,5-trimethoxybenzyl fragment connected to a 2,2'-bipyrimidine core via a 1,2,3-triazole unit and compound **1b** contains the same backbone as in **1a** substituted with three long alkyl chains.

Both molecules **1a** and **1b** were synthesized from 5-ethynyl-2,2'-bipyrimidine through the Cu(I)-catalyzed variant of the Huisgen 1,3-dipolar cycloaddition of azides and alkynes affording 1,2,3-triazoles (click chemistry; see Scheme 1).¹² Following reported procedures,¹³ the catalyst employed resulted from an *in situ* reduction of copper (II) sulfate with sodium ascorbate; but the reactions were carried out under biphasic conditions.

Scheme 1 Synthesis of ligands **1a,b**. Reagents and conditions: Na-ascorbate, CuSO₄, CH₂Cl₂/H₂O, RT, 50 % yield.

The synthesis of the octahedral monomeric complexes [Ti(**1a**)(**2**)₂] and [Ti(**1b**)(**2**)₂] (Chart 1) constructed around a TiO₄N₂ core was then undertaken. The complexes were obtained by following a well-established procedure^{9b} based on the exchange of the labile isopropanol ligands coordinating the metal centre in [Ti(**2**)₂(HOⁱPr)₂]¹⁰ by a nitrogen bidentate ligand (1 equiv.) as shown in eqn (1).

They were isolated with yields of *ca.* 72%. Single crystals of [Ti(**1a**)(**2**)₂] suitable for X-ray diffraction analysis were obtained when [Ti(**1a**)(**2**)₂] is dissolved in CHCl₃ and vapours of *n*-pentane are allowed to slowly diffuse in this solution. Concerning [Ti(**1b**)(**2**)₂], it was isolated as a fine powdered solid. Both complexes could be completely characterized by NMR, elemental analysis and mass spectrometry. We have noticed by ¹H NMR that both compounds are stable titanium (IV) complexes in CDCl₃, and TGA showed no significant weight loss from thermal degradation below 230–240°C for [Ti(**1b**)(**2**)₂], with 5% weight loss temperature as high as 330°C (ESI, Fig. S1). Importantly, these complexes could be analysed by TLC either on standardized alumina or on silica, leading to distinct yellow spots reflecting the good stability of these complexes on these supports. We even took advantage of these unusual stability for neutral titanium complexes to purify [Ti(**1b**)(**2**)₂] complex over alumina.

The TiO₄N₂ octahedral unit within the molecular structure of [Ti(**1a**)(**2**)₂] is depicted in Fig. 1. The complex crystallizes in a centrosymmetric space group, and the enantiomer represented is arbitrarily chosen as Δ . With regard to its structural features, it is rather close to [Ti(bpym)(**2**)₂] (bpym = 2,2'-bipyrimidine),^{9b} with an axial *aS* configuration of the biphenol ligand **2**. The metrical data are also similar: d(Ti–O) = 1.87 ± 0.04 Å, d(Ti–N) = 2.25 ± 0.03 Å, and an expectedly narrow N–Ti–N chelate angle (71.93(10)°) within a distorted octahedral geometry. The triazole is not coordinating, playing only the role of a linker between the chelating bipyrimidine and the trialkoxybenzyl group. It is coplanar with the pyrimidine rings.

Fig. 1 Solid-state molecular structure of [Ti(**1a**)(**2**)₂]. Ti atoms are in green, C atoms in grey, O atoms in red, N atoms in blue. Hydrogen atoms and solvents are omitted for clarity.

The basic unit of the single crystal structure consists in couples of enantiomers associated through triazolyl-bipyrimidine ligand sides and ligand **2** tips (Fig. 2). The bimolecular units arrange into molecular layers according to a rectangular herringbone lattice, and the staggered superposition of molecular layers designs the lamellar substructure of an orthorhombic cell. The assembling of the ligands rejects the trimethoxybenzyl groups to the periphery of the bimolecular units and it was thus easy to imagine that nanosegregated structures and mesomorphism could be obtained if methyl groups were substituted by long alkyl chains.

The DSC curves and POM observations demonstrate that a flowing and birefringent mesophase (Sm_{rec}) is effectively found for [Ti(**1b**)(**2**)₂], in a quite broad range (80°C) between solid state (Cr) and isotropic liquid phase (Iso) (Fig. 3). The POM textures are fluid (quite viscous) and birefringent, but display no characteristic defects useful to the identification of the mesophase type. The SAXS pattern of this mesophase displays a series of reflections from a lamellar periodicity, besides the scattering signature from lateral distances between molten chains, as well as the broadened reflections of a two-dimensional lattice formed by the lateral arrangement of complexes (ESI, Fig. S2). From SAXS, the lamellar periodicity is determined at *d* ≈ 43 Å.

Fig. 2 a) and b) Views of the single-crystal structure of $[\text{Ti}(\mathbf{1a})(\mathbf{2})_2]$, using Mercury software. a) The association into bimolecular units is effected through the triazolyl-bipyrimide segment sides and the ligand 2 tips, while the trimethoxybenzyl groups are rejected to opposite boundaries of bimolecular units. b) Right: complexes arrange in molecular layers that are superimposed into lamellae of two layers with crystallization solvent interlayers. Left: the layers are constituted by the arrangement of units of paired complexes (dotted line). c) and d) Schematic representations of the molecular self-organization. c) Right: schematic top of bimolecular units. Left: schematic side-view of bimolecular units. d) Left: rectangular herringbone arrangement of the bimolecular units constituting the molecular layers. Right: staggered superposition of the successive molecular layers into lamellae.

Fig. 3 Differential scanning calorimetry (DSC) and polarized optical microscopy (POM) analyses of $[\text{Ti}(\mathbf{1a})(\mathbf{2})_2]$. Left: DSC curves (cooling and second heating at

$5^\circ\text{C}.\text{min}^{-1}$); solid state (Cr) to mesophase (Sm_{rec}) transition: $T_{\text{onset}} = 70^\circ\text{C}$, $T_{\text{max}} = 82^\circ\text{C}$, $\Delta H = 20 \text{ J.g}^{-1} = 35 \text{ kJ.mol}^{-1}$; Sm_{rec} to isotropic liquid phase (Iso) transition: $T_{\text{onset}} = 152^\circ\text{C}$, $T_{\text{max}} = 160^\circ\text{C}$, $\Delta H = 15 \text{ J.g}^{-1} = 26 \text{ kJ.mol}^{-1}$. Right: POM textures at 100°C , after slow cooling from Iso.

A lamellar configuration with alternating layers of conjugated segments and molten chains is also the definition of a smectic phase, and the mesophase obtained for $[\text{Ti}(\mathbf{1b})(\mathbf{2})_2]$ was therefore ranked among these phases, notwithstanding that the complex shape is far from a calamitic mesogen. The indexation trials of the reflections converged to a rectangular lattice with parameters close to that of crystalline layers of $[\text{Ti}(\mathbf{1a})(\mathbf{2})_2]$ (Table S1). This finding indicates that the intercalation of the long alkyl chains between complexes erases the three-dimensional structure and alters the regularity of the in-plane arrangement, besides of conferring the fluidity to the mesophase, but that the way complexes are arranged is little affected. Both moieties are indeed separated by a sharp interface as demonstrated by the observation of lamellar reflections up to the fourth order, and they are therefore largely free to self-assemble in their optimal way within their respective layers. The lamellar configuration however introduces the constrain that the area per molecule is the same for all layers, whereas the cross-sectional area of the complexes ($149\text{-}150 \text{ \AA}^2$) is more than twice that of the three alkyl chains ($68\text{-}70 \text{ \AA}^2$). For the compensation of this discrepancy, an energy-costly mechanism might have been the lateral spreading and re-folding of the alkyl tails. The self-assembling process however follows a much more efficient way that preserves compact aliphatic layers and minimizes interface areas, namely the intercalation of the alkyl chains originating from neighbouring lamellae, which hence adopt a bilayer-monolayer configuration, as schematically represented in figure 4.

Altogether, two titanium (IV) complexes containing one trialkoxybenzyl-triazolyl-bipyrimidine and two 6,6'-diphenyl-2,2'-biphenolato ligands were synthesized and investigated upon their self-assembly properties. In the crystal phase obtained with methyl end-groups, the molecules were found to self-assemble through their ligands in bimolecular units arranging in superposed layers. The remarkable stability of the complexes allowed to study the thermotropic liquid crystal properties obtained with hexadecyl end-chains.

Fig. 4 Schematic view of the self-organization of $[\text{Ti}(\mathbf{1b})(\mathbf{2})_2]$ complexes in the smectic-like phase, derived from the crystal phase of $[\text{Ti}(\mathbf{1a})(\mathbf{2})_2]$, left: the constraints introduced by the packing of the long-alkyl chains replacing the methyl groups imply their rejection to the same side of bimolecular units; right: the bimolecular units arrange into bilayers with the alkyl chains forming intercalated monolayers with those originating from neighbouring lamellae. The alternation of molten chains layers and bilayers of complexes generates a smectic-like structure, which is defined by the lamellar periodicity $d = 43 \text{ \AA}$ and the organization within layers.

In the smectic-like mesophase of $[\text{Ti}(\mathbf{1b})(\mathbf{2})_2]$, the complexes arrange in a similar way as in the crystalline structure of $[\text{Ti}(\mathbf{1a})(\mathbf{2})_2]$, except the formation of intermediate layers of molten alkyl tails responsible for fluidity and mesomorphism. Although the architecture of these molecules is far from a rod-like unit, the bimolecular entities mimic smectogens, due to conformation and way of self-assembling rejecting the alkyl tails bearing segments to the

layer boundary. The smectic mesomorphism is further promoted by the bilayer-monolayer configuration offering balanced interface area and space requirement to complexes and chains.

In conclusion, this work demonstrates that the generation of a Ti(IV)-based mesogen is accessible; however this required a precise design to provide a good thermal and hydrolytic stability for the resulting architecture. Next, we envisage to generate more complex Ti(IV)-based mesogenic structures constructed around TiO_4N_2 motifs. Also, we anticipate that the combination of mesomorphic properties and titanium complexes should lead to an unprecedented class of materials where self-assembly is the key to access nanostructured functional Ti(IV)-based materials.

Conflicts of interest

There are no conflicts to declare.

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