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### Dinuclear Lanthanide Schiff-Base Complexes Forming a Rectangular Columnar Mesophase

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The Schiff base  $LH_3$  obtained by condensation of 3-formyl-4-hydroxyphenyl-3,4,5-tris(tetradecyloxy)benzoate with 1,3diamino-2-propanol reacts with lanthanide(III) acetate salts to form dinuclear complexes of the type  $Ln_2L_2$  with the trivalent ions from the first half of the lanthanide series (Ln = Nd, Sm, Gd). These stable and neutral metallomesogens exhibit a rectangular columnar mesophase over a broad temperature range.

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lumnar phase over a broad temperature range. Depending

on the radius of the lanthanide(III) ion, either dinuclear f-

d<sup>[7]</sup> or trinuclear f-d-f complexes were formed.<sup>[7,8]</sup> Note that

#### Introduction

N,N'-Bis(salicylidene)ethylenediamine (salen) and similar Schiff-base ligands derived from diamines other than ethylenediamine have often been used as building blocks for metal-containing liquid crystals.<sup>[1]</sup> This work was focused mainly on copper(II), nickel(II) or oxovanadium(IV) (vanadyl) complexes that exhibit smectic mesophases.<sup>[2,3]</sup> essentially smectic A and smectic C phases, but also the more ordered smectic E phase.<sup>[2e]</sup> Similar mesomorphic properties were also observed in calamitic cobalt(II) complexes,<sup>[2g]</sup> and the enhancement of the molecular anisotropy of such Ni<sup>II</sup>, Cu<sup>II</sup> and VO<sup>IV</sup> salen complexes by the use of alkylphenylazo groups results in new mesomorphic systems showing a high temperature SmC phase, and in some cases. the nematic phase.<sup>[4]</sup> Binnemans et al. reported the first mesomorphic lanthanide complexes of salen-type Schiff base, but owing to the elevated transition temperatures, unequivocal identification of the mesophase formed was not possible.<sup>[5]</sup> Swager and co-workers studied vanadyl complexes derived from such Schiff bases, possessing a hexacatenar structure, that exhibit a rich columnar mesomorphism,<sup>[6]</sup> whereas Binnemans et al. synthesized mixed f-d metallomesogens, derived form the related hexacatenar ligand, that contain both a transition metal ion and a lanthanide(III) ion.<sup>[7]</sup> These compounds showed a hexagonal co-

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all these complexes can be considered as adducts of a mesogenic Cu(salen) or Ni(salen) complex of a trivalent lanthanide ion. Because the Cu(salen) and Ni(salen) complexes are electrically neutral, three nitrate groups are necessary to compensate for the positive charge of the lanthanide ion in the resulting mixed f-d complexes. Additionally, if such a doubly negatively charged ligand is to be used to prepare purely lanthanide complexes, a further small inorganic anion (e.g. X = Cl, NO<sub>3</sub>) has to be present to obtain electric neutrality in the corresponding LnXL complexes, otherwise neutral complexes with a different stoichiometry such as Ln<sub>2</sub>L<sub>3</sub> type may be formed instead. By modifying the salentype Schiff-base ligand, it should be possible to obtain an organic species that contains three deprotonable OH groups and which can be used as triply negatively charged anionic ligand to form neutral complexes with the trivalent lanthanide cations. Such a ligand can be obtained by condensing the aldehyde that is used to prepare the salen-type Schiff base, with 1,3-diamino-2-propanol instead of 1,2-diaminoethane.

In this paper, we show that the chemical modification of the *salen*-type Schiff base by using 1,3-diamino-2-propanol instead of 1,3-diaminopropane in the reaction with the appropriate 3-formyl-4-hydroxyphenyl-3,4,5-tris(tetradecyloxy)benzoate appears to be a judicious approach to prepare neutral dinuclear complexes of the type  $Ln_2L_2$  with trivalent lanthanide ions. Moreover, these complexes are mesomorphic and exhibit a rectangular columnar mesophase over a large temperature range, as shown by smallangle X-ray diffraction. With the help of molecular mechanics, a model for the organization of these compounds in the columns is proposed.

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### **Results and Discussion**

The Schiff-base ligand LH<sub>3</sub> was obtained by condensation of the aldehyde 3-formyl-4-hydroxyphenyl-3,4,5-tris(tetradecyloxy)benzoate (1 equiv.) and 1,3-diamino-2-propanol (0.5 equiv.) in toluene, with azeotropic removal of the water. The three dinuclear lanthanide(III) complexes (Ln = Nd, Sm, Gd) were synthesized by reaction between the lanthanide acetate salt Ln(CH<sub>3</sub>COO)<sub>3</sub>·xH<sub>2</sub>O (1.1 equiv.) and the Schiff base (0.5 equiv.) in chloroform at refluxing temperature. The synthesis of ligand and complexes 1-3 is outlined in Scheme 1.

A schematic representation of the dinuclear lanthanide(III) complexes is given in Scheme 1 (compounds 1, 2, 3). Because each ligand carries a triple negative charge, the positive charge of the two trivalent lanthanide ions is counterbalanced and the dinuclear complexes are neutral; therefore no counterions are necessary. This is in contrast with



Scheme 1. Synthesis of the Schiff-base ligand and the corresponding dinuclear Ln–Ln complexes 1–3. Reagents and conditions: (a) RBr (3 equiv.),  $K_2CO_3$  (6 equiv.), DMF, KI (catalytic amount), reflux overnight; (b) NaOH, ethanol, reflux for 4 hours; acidification by dilute HCl solution; (c) DCC, DMAP, dichloromethane, 24 hours at room temp.; (d) 1,3-diamino-2-propanol (0.5 equiv.), glacial acetic acid (catalyst), toluene, Dean–Stark trap, 3 hours at reflux; (e) Ln(CH<sub>3</sub>COO)<sub>3</sub>·xH<sub>2</sub>O (1.1 equiv.), chloroform, reflux overnight.

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the f-d complexes with *salen*-type ligands,<sup>[7,8]</sup> the lanthanide complexes with salicylaldimine Schiff bases which have counterions such as nitrate groups.<sup>[1f,9,10]</sup> or lipophilic bis(benzimidazole)pyridine-based ligands.<sup>[11]</sup> The reasons why a dinuclear complex is formed instead of a mononuclear species are due to the tendency of the lanthanide(III) ions to achieve a high coordination number and to the nature of the ligand itself, auspicious to such a coordination mode (fused chelating parts). Typically, the coordination number of the trivalent lanthanide ions in coordination compounds is eight or nine. Also six-coordinate lanthanide(III) complexes are known, for example the tris( $\beta$ -diketonato)lanthanide(III) complexes. When the ligand does not offer a sufficient number of donor atoms to the lanthanide(III) ion to achieve a high coordination number, some of the donor atoms can coordinate in a bridging mode. Alternatively, adducts can be formed with Lewis bases, such as water molecules. Unfortunately, we were unable to obtain single crystals, so that the structure of the complex is still unknown. It was also not possible to grow single crystals of similar complexes with shorter alkyl chains and due to the presence of paramagnetic ions, <sup>1</sup>H NMR spectra of the complexes were not resolved. It is however unlikely to consider the structure of the dinuclear lanthanide(III) complex as totally flattened and planar (as drawn in Scheme 1) by simply considering the coordination chemistry of d and felements and entropic phenomena. The geometric preferences of lanthanides to adopt coordination numbers higher than six support that such extended planarity is absent, and that the ligands are wrapped around the metallic centers. Thus, a more energetically favorable structure for these dinuclear species would imply the ligand to be bent or Vshaped (due to the flexible spacer), and that they are either entwined around the two metal ions as in helicates<sup>[12-14]</sup> (Figure 1a,  $D_2$  symmetry) or coordinated to the two cations in such a way that a sandwich complex with a mesocate structure is formed (part b in Figure 1,  $C_{2h}$  symmetry).<sup>[13]</sup> Whatever the exact structure is, it has been shown recently for some M<sub>2</sub>L<sub>3</sub> complexes, that both species exist in equilibrium in solution, and the helicate to mesocate isomerization only requires inversion at one metal center,<sup>[15]</sup> and that this low-energy cost equilibrium may be generalized to other systems. The driving forces for the formation of helicates and/or mesocates result from the minimization of energy of the ultimate self-assembly. Such a formation depends on the metal-imposed (number and coordination geometry) and ligand-imposed constraints (type, nature of the spacer and distance between bridging units), as well as to some degree of pre-organization of the ligand. In the case of lanthanides, helicates mainly possess a three-stranded helicate Ln<sub>2</sub>L<sub>3</sub> structure (in such case, the two lanthanide ions are wrapped by three ligands), while mesocate complexes of the type  $M_2L_2$  – schematically shown in Figure 1, b – are common for both d and f elements.<sup>[13]</sup> For instance, Gelasco and Pecoraro described the crystal structure of a closely related dimeric manganese(III) complex of the Schiff base 1,3-bis(5nitrosalicylidenimino)-2-propanol:<sup>[16]</sup> this dimeric manganese complex has a  $\mu^2$ -alkoxy core with a symmetric environment for the manganese(III) ions. The authors showed that the ligands adopt a hairpin conformation and that two of them wrap the two metallic ions in an antiparallel mode to form the neutral mesocate  $Mn_2L_2$  complex as schematically drawn in Figure 1, b. This particular dimeric structure could be representative of the chelating mode of this type of ligand with two metallic nuclei and generalized to other dinuclear species. We have thus extrapolated this mode of chelation to the presently studied dinuclear lanthanide(III) complexes, the close proximity of the two sets of donor atoms of the bidentate bridging ligand, and the presence of the central hydroxy coordinating group slightly disfavoring the formation of the helicate structure at the expense to the mesocate one; this assumption is comforted by some molecular calculations, too (vide infra).



Figure 1. Schematic representation of the two possible structures given by the  $Ln_2L_2$  complexes. The two bischelate bent-like ligands, may entwine the two metallic species to form a double-stranded helicate (**a**,  $D_2$  symmetry) or sandwich the metal ions to form a non-helical *meso* structure or mesocate instead (**b**,  $C_{2h}$  symmetry).

In this model, the two lanthanide(III) ions are in a sixcoordinate environment, with the coordination polyhedron being a (distorted) octahedron. The two coordinating octahedral cages of the two lanthanide ions share a common edge, and the alkoxide group bridges the two lanthanide(III) centers (Figure 2). For a further investigation of the conformation of this dinuclear complex and to support the mesocate structure, molecular simulations were performed on both mesocate and helicate conformers (Gaussian 03, rb3lyp/3-21g\*\*). For compatibility with the calculation bases, the lanthanide(III) cations were replaced in these models by yttrium(III), chosen because of its great proximity to the lanthanide series (located just above the lanthanum in the periodic table of elements) and for the similarity of the ionic radius between Y<sup>III</sup> and Ln<sup>III</sup>. The minimization yielded two stable structures with an energetic gap of 44.9 kJ·mol<sup>-1</sup> in favor of the mesocate conformation. For both conformers in these theoretical structures (taken as isolated molecule in the gas phase), the angle formed by the phenyl groups of the ligands is quite wide in comparison with the manganese complex just mentioned,<sup>[16]</sup> but a search in the Cambridge Crystallographic Database shows that the very flexible salen-type ligand can be very distorted by packing constraints in condensed phase. It is then reasonable to propose that the present dinuclear lanthanide(III) complexes adopt preferentially a mesocate form, with the ligands in the hairpin conformation. Furthermore, with this assumption, the pinched ligand structure could be even more stabilized by intramolecular  $\pi$ -stacking of the benzoate rings (vide infra).



Figure 2. Minimized structure of the dinuclear diligand species (see text; purple: lanthanide cation; blue: nitrogen atom; red: oxygen atom, green: carbon atom. Hydrogen atoms have been omitted for clarity.).

The Schiff-base ligand LH<sub>3</sub> is itself mesomorphic, not totally unexpected, because of its polycatenar-like molecular structure, a priori compatible with mesophase formation.<sup>[17]</sup> Observation by polarizing optical microscopy (POM) indicated a monotropic liquid-crystalline phase behavior. On heating the sample, an isotropic liquid is obtained at 82 °C, which was confirmed by an intense endothermic peak transition (82 kJ·mol<sup>-1</sup>) in the first heating run of the DSC curve. Heating was continued above 100 °C without detecting additional thermal events, and the sample was then cooled down. At 62 °C, a phase transformation is detected by the growth of birefringent dendritic features from the isotropic liquid, remembering one of the typical texture of the hexagonal columnar phase (Figure 3). A peak of  $-2.50 \text{ kJ} \cdot \text{mol}^{-1}$  in the DSC curve corresponds to this monotropic phase transition. The phase remained stable down to room temperature. On second heating, the compound cleared straight into the isotropic liquid at 62 °C, that is 20 °C lower than during the first heating. Subsequent cooling and heating repeated the behavior of the second cycle so crystallization from a solvent must result in a crystalline form that needs to rearrange on heating before it clears into the isotropic liquid. The X-ray diffractogram of the mesophase registered on cooling the sample from the isotropic liquid does not contradict the mesophase assignment made by POM, nor gives conclusive information about the mesophase symmetry, and so the mesophase remains assigned from its optical texture alone. The pattern recorded at 50 °C on cooling showed only one single, but sharp and intense small-angle diffraction peak at ca. 38 Å, which was indexed as the [10] reflection of a 2D hexagonal lattice. The liquid-like order of the aliphatic chains was confirmed by the presence of the broad scattering at ca. 4.5 Å. To conclude, the optical texture shows enough evidence that a hexagonal columnar phase was formed (Figure 3), and the thermal properties of the ligand can be summarized as follows: Cr 82 (Col<sub>h</sub> 62) I.

The lanthanide(III) complexes 1-3 are also mesomorphic, and exhibit a mesophase over a temperature range of more than 100 °C. The clearing temperatures of the complexes could not be determined due to extensive decomposition well above 200 °C. The transition temperatures are summa-



Figure 3. Optical texture of hexagonal columnar phase formed by the Schiff-base ligand  $LH_3$  at 58 °C.

rized in Table 1. At room temperature, the complexes are in a semi-crystalline or *condis* (conformationally disordered) phase as revealed by XRD: only broad and diffuse scatterings were observed in the angular range of study ( $0 < 2\theta$  $< 35^{\circ}$ ). The halo in the wide angle part at 4.5 Å corresponds to the liquid-like order of the molten chains, whereas those in the small angle part, obtained within the ratio 1:2:3 (at ca. 30.5, 15.3, and 10.2 Å) indicate some short-range layering correlations of the system. This lamellar structure is formed again on subsequent cooling/heating runs, proving the high reversibility of the phase transformation and the good thermodynamic stability of this phase. Above 100 °C, and for the three dinuclear complexes, a change in the optical texture concomitant to a phase transformation was detected. However, the optical textures observed by microscopy were not sufficiently characteristic to permit the unambiguous identification of the mesophase. With regards to the molecular structure of the complexes, which resembles to that of related dinuclear complexes constructed from hexacatenar ligands, the mesophase is likely columnar.<sup>[18]</sup> The definitive mesophase identification was achieved by temperature-dependent X-ray diffraction. The XRD pattern of the neodymium(III) complex 1 at 200 °C, chosen as representative example for the three complexes, is shown in Figure 4 and the relevant data are summarized in

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Table 2. The X-ray pattern recorded at 200 °C was chosen instead of those recorded at lower temperatures as it provided the most suitable information. Indeed, the reflections appear to sharpen and to become more intense as the temperature was raised, a result of the temperature-induced micro-segregation. The pattern reveals two diffuse scattering halos (5 and 6) observed in the mid and wide-angle region. The halo at 4.5 Å (6), corresponds to the liquidlike order of the aliphatic chains and to the loose lateral interactions between rigid parts of the complex, whereas the other diffuse halo (5), corresponding to an average distance of ca 10 Å, very likely conveys to the existence of dimeric species (vide infra). In the small angle region, four large reflections were observed and indexed into a rectangular 2D lattice with the pairs of Miller's indices [hk] = [11], [20],[22] and [40] (Table 2). This pattern is typical for a centered rectangular lattice with a *c2mm* plane group. Since two indexations of the reflections are possible (only harmonics of the fundamental reflections were measured), we have chosen the most likely one (Table 2). The first option consists of chosing [11] = 26.0 Å and [20] = 38.25 Å, but this yields to a highly anisometric rectangular lattice, the parameters of which (a = 76.5 Å and b = 27.45 Å) are highly incompatible with the molecular dimensions (length, width and thickness) of the dinuclear complexes. In contrast, the other option ([11] = 38.25 Å and [20] = 26.0 Å), leads to lattice parameters that are more relevant here (a = 52.0 Å and b = 56.45 Å) and in agreement with the size of the complexes.

Table 1. Transition temperatures of the dinuclear lanthanide complexes.

Compound	Ln	Transition temperatures <sup>[a]</sup> [°C]
1	Nd Sm	$X \cdot 116 \cdot Col_r \cdot c2mm \cdot 257$ (dec.)
2 3	Gd	$X \cdot 108 \cdot Col_{r}$ - <i>c2mm</i> · 227 (dec.) X · 106 · Col_{r}- <i>c2mm</i> · 236 (dec.)

[a] X: semi-crystalline lamellar solid or *condis* (conformationally disordered) phase;  $Col_r$ -*c2mm*: rectangular columnar phase with the centered *c2mm* symmetry; dec.: decomposition.



Figure 4. X-ray diffractogram of neodymium(III) complex 1 at 200  $^{\circ}\mathrm{C}.$ 

The similarity of the lattice parameters a and b in this case expresses that the rectangular lattice is in fact nearly square-like, that is that the cross-section of the columnar hard core (i.e. constituted of the rigid molecular parts) is not so elliptic, but rather more circular instead. In order to

Table 2. XRD data of the neodymium(III) complex 1 at 200 °C.<sup>[a]</sup>

Reflection no.[b]	$d_{\exp}^{[c]}$	[hk]	<i>I</i> <sup>[d]</sup>	$d_{\rm theo}^{\rm [c]}$	Cell parameters <sup>[c,e]</sup>
1	38.25	[11]	vs	38.25	$Col_r - c2mm$
2	26.0	[20]	VS	26.0	a = 52.0  Å
3	19.1	[22]	m	19.1	$b = 56.4_5 \text{ Å}$
4	13.1 <sub>5</sub>	[40]	m	13.0	$S = 2.935 \text{ Å}^2$
5	10.0	-	broad	-	$V_{cell} = 14.675 \text{ Å}^3$
6	4.5		broad	-	$N_{col} = 2$

[a] For complexes 2 and 3, similar data were obtained: Sm complex 2: a = 52.2 Å, b = 56.3 Å,  $V_{mol} = 7360$  Å<sup>3</sup>,  $N_{col} = 2$ ; Gd complex 3: a = 52.4 Å, b = 56.1 Å,  $V_{mol} = 7380$  Å<sup>3</sup>,  $N_{col} = 2$ . [b] The numbering of X-ray reflections corresponds to the one in Figure 4. [c]  $d_{exp}$  and  $d_{theo}$  are the experimentally measured and theoretical diffraction spacings. Distances are given in Å. a, b are the parameters of the Col<sub>r</sub> phase, S is the lattice area and  $V_{cell}$  the volume of the rectangular cellule 10 Å thick. [d] Intensity of the reflection. vs: very strong, m: medium. [e] a, b are deduced from the measured spacings  $d_{11}$  and  $d_{20}$ :  $a = 2d_{20}$ ; b = A, with  $A = \sqrt{\frac{2}{\frac{1}{d_{11}^2} + \frac{1}{d_{11}^2} - \frac{1}{2d_{20}^2}}}$ ;

 $d_{\text{theor}}$  is deduced from the following mathematical expression and the lattice parameters *a* and *b*:  $\frac{1}{d_{hk}} = \sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2}}$ .  $S = a \times b$ , and  $V_{cell}$  $= \frac{1}{2} \times S \times 10$ .  $N_{col}$  is the aggregation number or the number of molecular equivalents per stratum of column 10 Å thick,  $N_{col} = V_{cell} / V_{mol}$ .

understand the molecular packing of the complexes in the columns and to propose a model, we first compared the molecular dimensions and volume with the columnar crosssection and rectangular cell volume of the Col<sub>r</sub> phase, and followed the methodology explained elsewhere<sup>[19]</sup> to evaluate the number of molecules per a given length of column, h. Of course, h can be chosen arbitrarily, but in the following calculation a value of 10 Å has been assumed, corresponding to the broad signal 5 seen in the X-ray pattern (vide supra), which suggests that there is a periodicity at this distance and the breadth of the signal that there is a correlation which persists over several molecules. The minimization of the complex also showed a thickness of about 10 Å, concordant with this assumption. Thus, from the molecular volumes  $V_{\rm mol}$  of the Ln<sub>2</sub>L<sub>2</sub> complexes (for Ln = Nd,  $V_{\rm mol}$  = 7340 Å<sup>3</sup> at 200 °C), it was found that two complexes molecular equivalents occupy the rectangular cell, 10 Å thick. Similar data were obtained for the corresponding dinuclear gadolinium and samarium complexes (see Table 2).

On the basis of the molecular minimization shown above (Figure 2), it is possible to consider the formation of a dimeric species which takes an overall "bow-tie" conformation, with a thickness of approximately 10 Å, and be stabilized by lateral intermolecular interactions between the phenyl rings of the ligand strands as shown in the Figure 5. This interaction, which depends on the molecular structure, is short range and is limited in the plane to a dimeric species only because of the important number of irradiating aliphatic chains ('bow-tie'-like dimer, Figure 5), which results in the strong curvature of the hard-flexible interface and disfavors molecular associations higher than in pairs. The formation of columnar stacking is mainly driven by the

micro-segregation between the hard and flexible parts (Figure 6). The hard part of the dimer forms the rigid spine of the column, and the voids between these "hard" columns is filled by the homogeneous matrix of aliphatic chains. The stability of the edifice is mainly ensured by weak van der Waals interactions and by inter-dimeric interactions along the columnar axis (Figure 6). These columns then self-organize into the 2D rectangular lattice (Figure 7). A molecular dynamics model has been built from two dimers disposed respectively on the edge and at the center of a rectangular cell based on the parameters determined by XRD. Due to the incompatibility of the lanthanide ions with common forcefields used for organic compounds, and according to our previous discussion about the shape of these salen-type dimetallic complexes, the geometry of the central part of the complex was tethered to a template structure obtained from the crystallographic data of the dinuclear manganese complex mentioned above.<sup>[15]</sup> Nevertheless, each molecule was allowed to move freely from each other within the cell



Figure 5. The 'bow-tie'-like dimeric species viewed along the columnar axis (i.e. cross-section of column).



Figure 6. View of the stacking along the columnar axis, with the stacking periodicity, h, also representing the molecular thickness.

during the simulation. This model led to a consistent result, with a density of the packing very close to unity, similar to that of the mesophase.



Figure 7. Arrangement of the 'bow-tie'-like dimers within the 2D rectangular lattice.

### Conclusions

In this paper, we report the first examples of neutral, liquid-crystalline dinuclear f-f complexes, i.e. complexes that contain two lanthanide ions. The ligand was designed in such a way that the resulting complexes are electrically neutral, so that no additional inorganic or organic counterions are needed to counterbalance the electric charges of the complex. Due to the synthetic methodology specifically elaborated here, only homodinuclear f-f complexes were prepared. The complexes exhibit a rectangular columnar mesophase, and a model, based on X-ray diffraction data and molecular modelling, is proposed for the molecular self-organization.

### **Experimental Section**

Techniques: The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz) and on a Bruker AMX-400 (operating at 400 MHz), using CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as internal standard. The NMR shifts were assigned with the help of <sup>13</sup>C DEPT spectroscopy, two dimensional correlation spectroscopy (COSY) and proton-carbon heteronuclear multiple-quantum coherence (HMQC) spectroscopy. FTIR spectra were recorded on a Bruker IFS-66 spectrometer, using the KBr pellet method. Elemental analyses were obtained on a CE-Instrument EA-1110 elemental analyzer. MALDI-TOF mass spectra were measured on a VG Tofspec SE (Micromass, UK) equipped with a N<sub>2</sub>-laser (337 nm). Optical textures of the mesophases were observed with an Olympus BX60 polarizing microscope equipped with a LINKAM THMS600 hot stage and a LINKAM TMS93 programmable temperature-controller. DSC traces were recorded with a Mettler- Toledo DSC821e module. The XRD patterns were obtained with two different experimental set-ups, and in all cases, the powdered sample was filled in Lindemann capillaries of 1 mm diameter. A linear monochromatic Cu-K $\alpha_1$  beam ( $\lambda = 1.5405$  Å) obtained with a sealed-tube generator (900 W) and a bent quartz monochromator were used (both generator and monochromator were manufactured by Inel). One set of diffraction patterns was registered with a curved counter Inel CPS 120, for which the sample temperature is controlled within  $\pm 0.05$  °C; periodicities up to 60 Å can be measured. The other set of diffraction patterns was registered on Image Plate. The cell parameters are calculated from the position of the reflections at the smallest Bragg angle, which are in all cases the most intense. Periodicities up to 90 Å can be measured, and the sample temperature is controlled within ±0.3 °C. The molecular modeling calculations were performed on a SGI Origin 2800 20 CPU computer and on an SGI Octane<sup>2</sup> calculators using Insight II and Discover 3 software from Accelrys (www.accelrys.com) with the cvff forcefield. For all models, prior to the dynamics, the systems were minimized to a gradient of 0.05 kcalmol<sup>-1</sup>. The simulation then consisted of a 200 ps isotherm at 473 K in the NVT-PBC ensemble and with a 1 fs time step.

Synthesis of the Schiff-Base Ligand LH3: The aldehyde 3-formyl-4-hydroxyphenyl-3,4,5-tris(tetradecyloxy)benzoate was synthesized as described elsewhere.<sup>[7]</sup> To a solution of 3-formyl-4-hydroxyphenyl-3,4,5-tris(tetradecyloxy)benzoate (1.33 g, 0.002 mol) in 200 mL of toluene was added 1,3-diamino-2-propanol (90 mg, 0.001 mol) and 5 drops of glacial acetic acid (as the catalyst). The mixture was heated for 3 hours at reflux and water formed by the reaction was removed azeotropically (Dean-Stark trap). After allowing the solution to cool down to room temperature, the solvent was removed at reduced pressure. The crude product was purified by crystallization from absolute ethanol. Yield: 80% (1.11 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.89$  (m, 18 H, CH<sub>3</sub>), 1.20–1.40 (m, 120 H, CH<sub>2</sub>), 1.49 (m, 12 H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O), 1.70-1.90 (m, 12 H, CH2-CH2-O), 3.70-3.95 (m, 4 H, N-CH2), 4.05 (m, 12 H, CH2-O), 4.30 (m, 1 H, CH), 7.01 (d, 2 H, H<sub>arom</sub>), 7.14 (s, 2 H, H<sub>arom</sub>), 7.16 (d, 2 H, H<sub>arom</sub>), 7.39 (s, 4 H<sub>arom</sub>), 8.40 (s, 2 H, CH=N), 13.0 (br., OH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 14.1 (CH<sub>3</sub>), 22.7 (CH<sub>2</sub>), 26.1 (CH<sub>2</sub>), 29.3-30.3 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 63.3 (CH<sub>2</sub>-N), 69.3 (CH<sub>2</sub>-O), 70.5 (CH), 73.6 (CH<sub>2</sub>-O), 108.7 (C<sub>arom</sub>), 117.9 (C<sub>arom</sub>), 118.5 (Carom), 123.7 (Carom), 123.9 (Carom), 126.2 (Carom), 158.8 (C=O), 166.7 (C=N) ppm. IR (KBr):  $\tilde{v} = 1641$  (C=N), 1201 (C-O) cm^{-1}.  $C_{115}H_{194}N_2O_{13}$  (1812.78): calcd. C 76.19, H 10.79, N 1.55; found C 76.18, H 10.99, N 1.42.

Synthesis of the Lanthanide(III) Complexes: The dinuclear lanthanide complexes (Ln = Nd, Sm, Gd) of the Schiff-base ligand LH<sub>3</sub> were synthesized by reaction between the lanthanide acetate salt  $Ln(CH_3COO)_3 \cdot xH_2O$  (1.1 equiv.) and the Schiff base (1 equiv.) in chloroform at refluxing temperature overnight. The acetate ions act as the base to deprotonate the ligand. The complexes were purified by crystallization from a water/ethyl acetate mixture, and were obtained in moderate yields: 74% for the Nd complex 1, 62% for the Sm complex 2 and 49% for the Gd complex 3. MALDI-TOF measurements show a molecular peak that corresponds to the dinuclear species with the stoichiometry [Ln<sub>2</sub>L<sub>2</sub>] for the neodymium(III) and samarium(III) complexes.

Nd Complex 1:  $C_{230}H_{382}N_4Nd_2O_{26}$  (3907.99): calcd. C 70.69, H 9.85, N 1.43; found C 70.79, H 9.84, N 1.44. MALDI-TOF:  $M_w$ (isotopic) = 3907.68 *m/e*;  $M_w$ (found) = 3909.30 *m/e*. IR (KBr):  $\tilde{v} = 1633$  (C=N) cm<sup>-1</sup>.

**Sm Complex 2:** C<sub>230</sub>H<sub>382</sub>N<sub>4</sub>O<sub>26</sub>Sm<sub>2</sub> (3920.23): C 70.47, H 9.82, N 1.43; found C 69.97, H 9.69, N 1.41. MALDI-TOF: *M*<sub>w</sub>(isotopic)

= 3920.71 *m/e*;  $M_w$ (found) = 3921.65 *m/e*. IR (KBr):  $\tilde{v}$  = 1633 (C=N) cm<sup>-1</sup>.

**Gd Complex 3:**  $C_{230}H_{382}Gd_2N_4O_{26}$  (3934.01): C 70.22, H 9.79, N 1.42; found C 69.67, H 9.96, N 1.34. IR (KBr):  $\tilde{v} = 1633$  (C=N) cm<sup>-1</sup>.

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