Adducts of Schiff Bases with Tris(β-diketonato)lanthanide(III) Complexes: Structure and Liquid-Crystalline Behaviour

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Adducts of the Schiff base 2-hydroxy-*N*-octadecyloxy-4-tetradecyloxybenzaldimine with tris(β-dibenzoylmethanato)-lanthanide(III) complexes are described. The stoichiometry of the complexes is $[Ln(dbm)_3L_x]$, where Ln is a trivalent lanthanide ion (all lanthanides except Ce and Pm), Hdbm is dibenzoylmethane and L is the Schiff base; x = 2 for Ln = La–Er and x = 1 for Ln = Tm–Lu. The Schiff-base ligands are in a zwitterionic form and coordinate through the phenolic oxygen only. The X-ray single-crystal structure of $[La(dbm)_3L'_2]$ with *L'* = *N*-butyl-2-hydroxy-4-methoxybenzaldimine is described. The solution structure of lanthanum(iii) complexes has been investigated by 1D and 2D ^{1}H NMR techniques. Although the long-chain Schiff-base ligand and the tris(β-dibenzoylmethanato)lanthanide(III) complexes are non-mesomorphic, some of the adducts exhibit a monotropic smectic A phase. The mesomorphic behaviour depends on the lanthanide ion, in the sense that only a mesophase is observed for the series Ln = La–Eu, not for the heavier lanthanides.

Introduction

Tris(β-diketonato)lanthanide(III) complexes are well-known as NMR shift reagents.[1−3] Examples are $[Pr(fod)_3]$ and $[Eu(fod)_3]$ (fod = anion of 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione). The shift of the proton resonances is related to the fact that organic molecules with free electron pairs (i.e. Lewis bases) can form adducts with the tris-β-diketonate complexes of paramagnetic and magnetically anisotropic lanthanide(III) ions. The coordination sphere of the lanthanide ion in a tris(β-diketonato)lanthanide(III) complex is unsaturated, since the coordination number of the metal ion in these complexes is only six, whereas lanthanide ions prefer to be coordinated to eight or nine donor atoms.[4] The lanthanide ion in the tris-β-diketonate complexes can expand its coordination sphere by forming adducts with neutral molecules containing oxygen- or nitrogen-donor atoms. Such a molecule can be water, and therefore the tris(β-diketonato)lanthanide(III) complexes can easily be transformed into bis(hydrates). However, polydentate ligands (e.g. 1,10-phenanthroline) can replace water in the first coordination sphere, and the resulting lanthanide complexes often show a strong photoluminescence. A typical example of a luminescent lanthanide complex is $[Eu(tfa)_3(phen)]$, (tta = anion of thenoyltrifluoroacetone, phen = 1,10-phenanthroline).[5−7] These luminescent complexes can find application in organic light-emitting diodes (OLEDs).[8] Binnemans and Moors have shown that Lewis-base adducts of tris(β-diketonato)lanthanide(III) complexes can be doped into a nematic liquid-crystal mixture to obtain luminescent liquid crystals.[9] Hapiot and co-workers obtained similar results by doping cholesteryl alkanoate adducts of $[Eu(tta)_3]$ into a cholesteric liquid crystal.[10,11] Of course, it would be interesting to design lanthanide β-diketonate complexes that exhibit a liquid-crystalline phase themselves, rather than relying on host-guest systems. Earlier trials to prepare liquid-crystalline lanthanide complexes with β-diketonate ligands were unsuccessful,[12] but recently two new independent approaches gave encouraging results. Galyametdinov and co-workers made monotropic liquid-crystalline lanthanide complexes starting from mesomorphic β-diketone ligands.[13] Binnemans and Lodewyckx reported in a communication on a monotropic smectic A mesophase in adducts of salicylaldimine Schiff bases to $[Ln(dbm)_3]$ complexes (dbm = anion of dibenzoylmethane).[14] In these compounds, neither the Schiff base nor the tris(β-diketonato)lanthanide(III) complex exhibit a mesophase, but the resulting bisadducts are liquid crystalline. It should be noted that the Schiff bases are the same as the ones which have been used in the past to synthesise liquid-crystalline lanthanide complexes with Schiff-base ligands.[15−18]

In the work of Binnemans and Lodewyckx,[14] the compounds were not structurally characterised, and the mesophase was investigated by polarising optical microscopy

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only. In this paper, we give a detailed description of the structural and thermal properties of Schiff-base adducts of tris(dibenzoylmethanato)lanthanide(III) complexes. The crystal structure of an adduct of a Schiff base with short alkyl chains to $[La(dbm)_3]$ is described. The solution structure of diamagnetic complexes was investigated by 1D and 2D ^1H NMR methods. A series of compounds was prepared in order to investigate the influence of the lanthanide ion on the thermal properties (Figure 1). The thermal behaviour of the lanthanide complexes was investigated by polarising optical microscopy (POM), differential scanning calorimetry (DSC) and by time-resolved temperature-dependent synchrotron X-ray diffraction measurements at the DUBBLE-beamline of the ESRF (Grenoble, F).

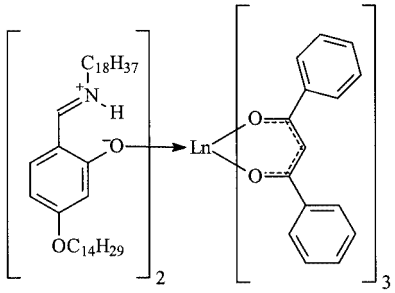

Figure 1. Schematic structure of the $[Ln(dbm)_3L_2]$ complexes

Results and Discussion

Synthesis

The Schiff-base ligands were prepared according to a literature method.[15] The tris(dibenzoylmethanato)lanthanide(III) complexes were synthesised in an ethanolic solution by first transforming dibenzoylmethane Hdbm (1,3-diphenyl-1,3-propanedione) into its sodium salt by reaction with sodium hydroxide. Secondly, the tris complexes were precipitated out of solution by addition of an aqueous solution of the corresponding lanthanide nitrate to the solution of the sodium salt of dibenzoylmethane. After drying the tris(dibenzoylmethanato)lanthanide(III) complex in a vacuum oven, the anhydrous compound was redissolved in absolute ethanol and added to two equivalents of the Schiff base dissolved in absolute ethanol. The adducts precipitated immediately. All the adducts were bisadducts (two Schiff bases bound to one lanthanide ion) whereas monoadducts were obtained for the lanthanide ions at the end of the series: thulium, ytterbium and lutetium. These ions have the smallest ionic radii among the trivalent lanthanide ions and therefore show less tendency to expand their coordination sphere. The complexes were characterised by CHN analysis and by infrared spectroscopy. The main difference between the mono- and the bis adducts is the position of the C=N stretching vibration: 1604−1606 cm^{-1} for the monoadducts and 1647−1653 cm^{-1} for the bis adducts. The stoichiometry of the complexes was not influenced by the ratio $[Ln(dbm)_3]/L$. We worked with a 1:1 ratio, so that $[Ln(dbm)_3]$ was present in excess. Complexes of all the lanthanide ions except cerium and promethium were prepared. Additionally, the lanthanum complex of the small Schiff-base ligand with methoxy and butyl chain (*N*-butyl-2-hydroxy-4-methoxybenzaldimine) was prepared for the growth of single crystals.

Crystal Structure

The X-ray single-crystal structure of $[La(dbm)_3L'_2]$ with L′ = *N*-butyl-2-hydroxy-4-methoxybenzaldimine was determined (Figure 2). According to the crystal structure, the Schiff bases coordinate as neutral ligands to the La^{III} ion i.e. the oxygen atoms of the OH group are deprotonated and the hydrogen atoms have been transferred to the nitrogen atoms. As a consequence, a zwitterionic structure (negative charge on the oxygen atom, positive charge on the imine nitrogen atom) is generated. The coordination polyhedron of the La^{III} ion, which can be described as a distorted bicapped trigonal prism, is built up of eight oxygen atoms (six oxygen atoms of the three dibenzoylmethanato ligands and two oxygen atoms of the two Schiff bases). Intramolecular N−H···O hydrogen bonds appear between the protonated nitrogen and the deprotonated oxygen atoms [average H···O distance: 1.989(8) Å]. One hydrogen (on N63) forms a second, but longer, H bond with an oxygen atom (O23) of a dibenzoylmethanato ligand [H···O distance: 2.429(5) Å]. The dihedral angle between the phenyl rings of the two Schiff-base ligands is 87.2(2)°, so the phenyl rings are positioned nearly perpendicular to each other. Both butyl chains of the Schiff bases are in the all-*trans* conformation. The dibenzoylmethanato ligands are considerably distorted: the maximum dihedral angle observed between two phenyl planes of this ligand is 24.0(2)°. A

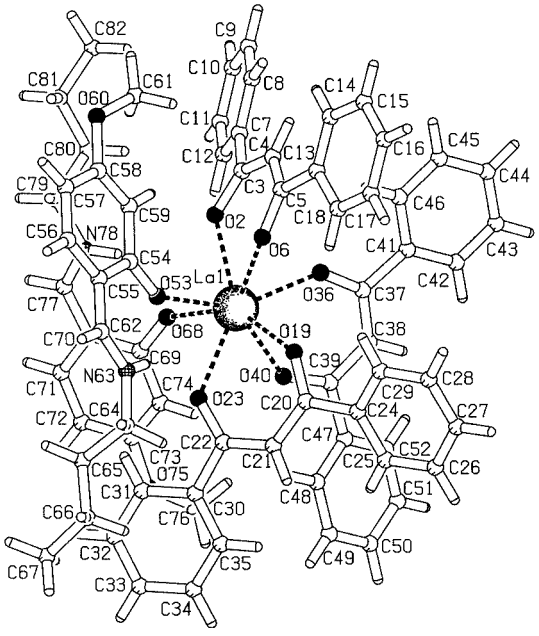

Figure 2. Molecular structure of $[La(dbm)_3L'_2]$, where L′ = *N*-butyl-2-hydroxy-4-methoxybenzaldimine

slight stacking of phenyl rings is noticed in the packing: the shortest ring···ring distance [3.948(3) Å] is found between ring C41−C46 and ring C47−C52 of a symmetry-related complex generated by [1 − *x*, 1 − *y*, 1 − *z*]. A void of 100 Å^3 at position (0, 1/2, 1/2) contains diffuse solvent.

Structure in Solution

The coordination mode of the lanthanide ion in solution was examined by measuring one- and two-dimensional proton NMR spectra of the [La(dbm)$_3$] and [La(dbm)$_3$L$_2$] complexes (L = 2-hydroxy-*N*-octadecyloxy-4-tetradecyloxybenzaldimine) and comparing them with the ^{1}H NMR spectra of the Schiff-base ligand L and the β-diketone Hdbm. A list of all NMR resonances is given in the Exp. Sect. The proton resonances of the free ligands are sharp and show the expected splitting pattern, with the exception of the phenolic proton resonance of L, which is extremely weak and broad, due to its fast exchange with the solvent. Surprisingly, the ^{1}H NMR spectrum of the [La(dbm)$_3$L$_2$] complex at room temperature shows that the proton resonances of the dbm ligand appear as broad humps, while the proton resonances of the Schiff base L in [La(dbm)$_3$L$_2$] appear as well-resolved peaks (Figure 3). The dbm proton resonances are also very broad in the parent [La(dbm)$_3$] complex, implying either the presence of different conformers in the solution which undergo dynamic exchange, or the presence of two different modes of dbm binding to the La^{III} ion. Variable temperature ^{1}H NMR spectra of both [La(dbm)$_3$] and [La(dbm)$_3$L$_2$] complexes were measured in order to investigate the dynamic process which leads to the broadening of the dbm resonances. When the temperature of the [La(dbm)$_3$] solution was lowered to 258 K, two resolved sets of dbm peaks could be detected. The larger set of peaks, at δ = 6.85, 7.42, 7.92 and 15.52 ppm, was assigned to the free Hdbm ligand, which was confirmed by independently recording the ^{1}H NMR spectrum of the free Hdbm ligand at the same temperature. Clearly, at low temperatures the dissociation of the [La(dbm)$_3$] takes place, and at 258 K almost 95% of the complex is dissociated. However, in the [La(dbm)$_3$L$_2$] complex, dissociation at low temperatures occurs to a much smaller extent, and at 258 K only about 10% of the Hdbm ligand is dissociated from the La^{III} ion. It is likely that the adduct formation with the L ligand stabilises the binding of dbm to the central lanthanide ion.

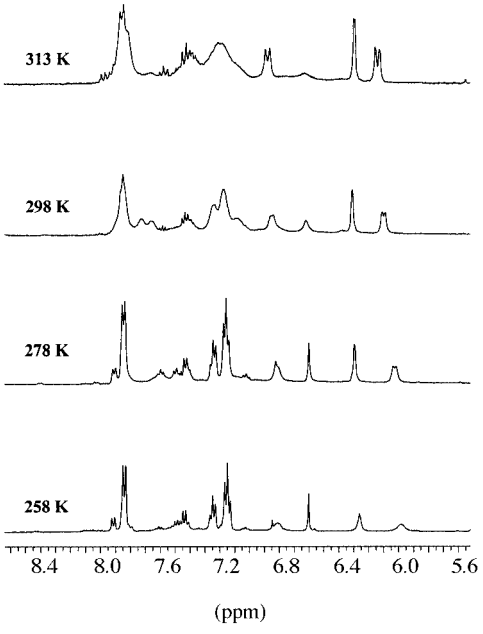

Figure 3. ^{1}H NMR spectra (400 MHz) of [La(dbm)$_3$L$_2$] in CD_2Cl_2 at different temperatures; at 313 K, the aromatic resonances of Schiff-base ligand L appear at δ = 6.16, 6.29 and 6.87 ppm; the broad humps at ca. δ = 6.65, 7.20 and 7.85 ppm belong to the diketonate ligand

The solid-state structure of the [La(dbm)$_3$L′$_2$] complex reveals the presence of intramolecular hydrogen bonding in the Schiff-base ligand. This hydrogen bonding, which occurs between the phenolic oxygen and the protonated imino nitrogen, is also found in solution. A strong, broad peak at δ = 13.3 ppm, which occurs upon complexation of the Schiff base to La^{III}, is a clear indication of the hydrogen bonding. Although the solid state structure of [La(dbm)$_3$L$_2$] suggests that the ligand L binds in a zwitterionic form, the two-dimensional ^{1}H NMR correlation spectroscopy (COSY), which was successfully used to confirm the presence of zwitterionic form of the Schiff ligand in related [LnL$_3$Cl$_3$] complexes,[19] gave no evidence that in the solution the phenolic proton has been completely transferred to the imino nitrogen. The absence of coupling between the proton at δ = 13.3 ppm and either the CH=N or N−CH$_2$ protons suggests that two extreme forms are in fast exchange: one in which the proton is bound to the phenolic oxygen, and the other in which this proton has been completely transferred to the imino nitrogen. Due to this exchange process, which takes place in the complex in solution, the N−**CH$_2$** protons appear as a broad peak (*FWHM* = 31 Hz). Even at 258 K this exchange is too fast on the NMR time scale for the two extreme forms to be distinguished by 2D COSY NMR spectroscopy.

Thermal Properties

The thermal behaviour of the complexes [Ln(dbm)$_3$L$_x$] was investigated by differential scanning calorimetry (DSC), polarising optical microscopy (POM) and high-temperature X-ray diffraction in a time-resolved mode. It should be noticed that neither L or [La(dbm)$_3$] are mesomorphic: the melting point of L is 73 °C and [La(dbm)$_3$] decomposes when heated in air.

Upon heating, [La(dbm)$_3$L$_2$] melts at 95 °C to an isotropic liquid. Upon cooling, a monotropic mesophase is formed at 81 °C. This mesophase was identified as a smectic A phase (SmA) by the typical defect texture (Figure 4): when cooling the isotropic liquid, bâtonnets formed at the clearing point and they coalesced to the focal-conic texture (fan texture). The rather low viscosity of the mesophase gives an indication that a real mesophase is present and not a plastic crystal phase. The mesophase ordering could be frozen into a glassy state. In the mesophase, the X-ray diffractograms show sharp Bragg reflections in the small angle region. The *d*-spacing values are in the ratio 1:1/2:1/3...1/*n*,

pointing to the presence of a lamellar structure. In most of the measurements only the first-order peak and a very weak second-order peak are observable. Higher orders can be detected after longer measuring times. The *d*-spacing does not show a pronounced temperature dependence. The broad halo in the wide angle region (at $d = 4.6$ Å) shows that the alkyl chains are in a molten state. These results support identification of the phase as a smectic A phase. The *d*-spacing (ca. 27.0 Å) is much smaller than the calculated length (45.5 Å) of the Schiff-base ligand in the fully extended (all-*trans*) conformation. The most probable explanation is an interdigitation of the alkyl chains of molecules situated in adjacent smectic layers, as this is an efficient way of space filling. No major changes are seen in the X-ray diffractograms when the sample is cooled to room temperature. This is an indication that the mesophase order is frozen into a glassy state and is in agreement with the observations made on the polarising optical microscope. X-ray diffractograms of $[La(dbm)_3L_2]$ at different temperatures are shown in Figure 5.

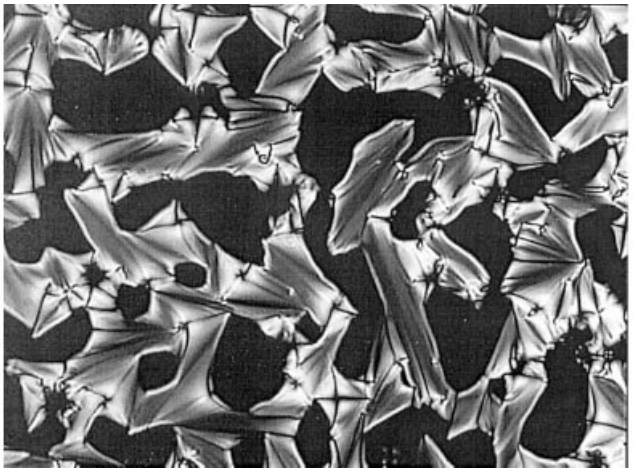

Figure 4. Texture observed for the smectic A mesophase of $[La(dbm)_3L_2]$ at 81 °C (clearing point)

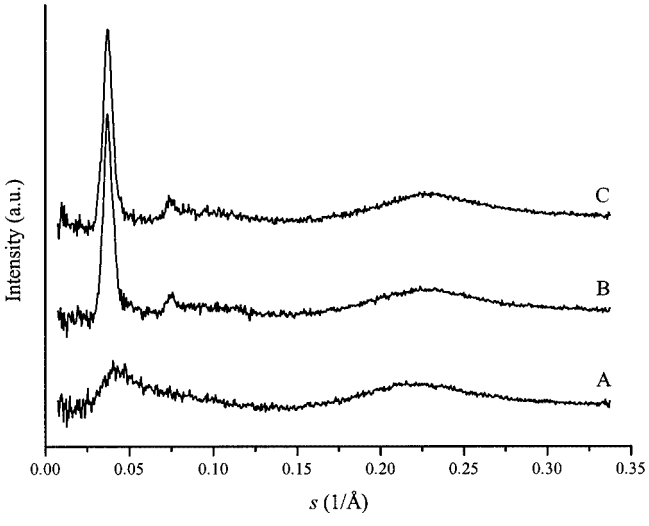

Figure 5. X-ray diffractograms for $[La(dbm)_3L_2]$. A: in isotropic liquid, B: in mesophase, C: at room temperature

The thermal behaviour of the complexes $[Ln(dbm)_3L_2]$ (Ln = Pr, Nd, Sm, Eu) resembles that of $[La(dbm)_3L_2]$ (Table 1). Hardly any variation is observed for the melting point and all these complexes form a monotropic smectic A phase. However, the temperature interval between the melting point and the clearing point becomes larger and larger when the size of the lanthanide ion decreases: $\Delta T =$ 12 °C for $[La(dbm)_3L_2]$, but $\Delta T = 30$ °C for $[Eu(dbm)_3L_2]$. The compounds of the heavier lanthanides do not form a mesophase; crystallisation occurs before a mesophase can be formed. It was difficult to decide whether or not $[Gd(dbm)_3L_2]$ and $[Tb(dbm)_3L_2]$ exhibit a mesophase, because bâtonnet-like features were observed during cooling of the melt. However, these features turned out to be very fine crystals floating in the melt. In contrast, $[Dy(dbm)_3L_2]$ and the other compounds in the lanthanide series did exhibit fast crystallisation without first forming tiny crystals. The melting point gradually decreases over the lanthanide series, with a discontinuity between Er^{III} and Tm^{III}. This can be attributed to the fact that a change in stoichiometry occurs between Er^{III} and Tm^{III} in the sense that the compounds at the end of the series contain only one Schiff-base ligand, not two.

Table 1. Transition temperatures of the $[Ln(dbm)_3L_x]$ complexes ($x = 2$ for La−Er, $x = 1$ for Tm-Lu)

Ln	Transition[a]	Temperatures (°C)
La	Cr → I	95
	I → SmA	81
Pr	Cr → I	94
	I → SmA	75
Nd	Cr → I	93
	I → SmA	71
Sm	Cr → I	93
	I → SmA	64
Eu	Cr → I	90
	I → SmA	60
Gd	Cr → I	86
Tb	Cr → I	80
Dy	Cr → I	74
Ho	Cr → I	72
Er	Cr → I	67
Tm	Cr → I	73
Yb	Cr → I	72
Lu	Cr → I	69

[a] Cr = crystalline solid; I = isotropic liquid; SmA = smectic A mesophase

These compounds are of special importance, because they form a quite unusual class of metal-containing liquid crystals (metallomesogens). It is a paradigm in metallomesogen research that in order to obtain high coordination number calamitic metallomesogens, one needs to make ligands with a very extended rigid rod-like core, or to incorporate a large number of long terminal alkyl chains.[20] None of the conditions is fulfilled in the case of the metal complexes described in this study, but nevertheless we observed a well-characterised low viscous mesophase for several of our compounds. Even more remarkable is the fact that although the size of the $[Ln(dbm)_3]$ complexes are not

much less than that of fullerene C_{60}, it is much easier to induce a mesophase in the lanthanide complexes.[21,22] Of course, however, the [Ln(dbm)$_3$] complexes are not as space-filling as C_{60}, in the sense that free space is present between the dibenzoylmethane rings.

Conclusions

The tris(dibenzoylmethanato)lanthanide(III) complexes can form Lewis-base adducts with long-chain salicylaldimines. The number of Schiff bases bound to a metal complex depends on the size of the lanthanide ion: two for most of the lanthanides and one for the ions at the end of the lanthanide series (Tm, Yb, Lu). The molecular structure and crystal structure of an adduct of [La(dbm)$_3$] with a short-chain Schiff base were determined, and this shows that the Schiff bases line up parallel to one another. Both the X-ray crystal structure and NMR spectroscopic data show that the Schiff base in the adducts is present in a zwitterionic form. Both the stoichiometry and the thermal behaviour of the complexes depend on the size of the lanthanide ion. The complexes [Ln(dbm)$_2$L$_2$] of the series Ln = La−Eu exhibit a monotropic smectic A phase. The temperature difference between the melting point and the clearing point of the monotropic mesophase increases over the lanthanide series. The complexes of the heavier lanthanides are not liquid-crystalline. Having determined the influence of the lanthanide ion on the thermal behaviour, further studies will focus on the influence of length of the alkyl and alkoxy chain of the Schiff base and on the influence of the type of 1,3-diketone.

Experimental Section

General: ^{1}H NMR spectra were recorded with a Bruker Avance 300 and a Bruker AMX-400 spectrometer. In variable-temperature experiments the temperature error was within 0.1 K. Two-dimensional correlation spectroscopy (COSY) was used as a tool to confirm the assignment of the proton resonances. CHN elemental analyses were performed on a CE Instruments EA-1110 elemental analyser. FTIR spectra were recorded with a Bruker IFS-66 spectrometer, using the KBr pellet method. The optical textures of the mesophase were observed with an Olympus BX60 polarised optical microscope equipped with a Linkam THMS-600 hot stage and a Linkam TMS-93 programmable temperature-controller. Synchrotron X-ray measurements were made on the DUBBLE-beam line (BM26) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France).[23,24] Intensities at scattering angles between 0.134° and 6.00° were collected with a quadrant-type detector at 0.70 m from the sample.[25] Distances in real space between 133 and 2.97 Å could be covered by using an X-ray wavelength of 0.62 Å (E = 20 keV). Flat samples of 1 mm thick, placed in a brass mould and covered by aluminium foil, were mounted in a Linkam THMS600 hot stage for temperature control. The heating rate used was 10 °C min^{-1} throughout. Scattering patterns were collected sequentially for six seconds, corresponding to one pattern for each degree centigrade in the temperature ramp. The scattering angles were calibrated using the reflections of silver behenate at room temperature. No corrections were performed to account for the use of a flat detector. Data were corrected for the detector response and normalised to the intensity of the primary beam, measured at the detector position. For data reduction the XOTOKO program was used.[26]

Crystallography: Yellow crystals of [La(dbm)$_3$L′$_2$] were obtained by slow evaporation of a solution of the complex in a CH_2Cl_2/EtOH mixture. A crystal of dimensions 0.25 × 0.15 × 0.10 mm^3 was mounted in a nylon loop for data collection at 110 K on a MAR diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) and which was equipped with a 300 mm imaging plate detector. The images were interpreted and intensities integrated with the program DENZO.[27] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.[28] Non-hydrogen atoms were refined anisotropically and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2-times U(eq) of the parent atoms (1.3-times for methyl groups). The disordered solvent in the void of 100 Å^3 at position 0, 1/2, 1/2 was modelled with SQUEEZE[29] (contribution of 13 electrons). Data: formula: $C_{69}H_{67}LaN_2O_{10}$; M_r = 1223.16; crystal system: triclinic, space group $P\bar{1}$, a = 10.9860(5), b = 15.4480(8), c = 19.1880(9) Å, α = 108.840(3), β = 94.240(3), γ = 103.960(4)°, V = 2949.8(2) Å^3, Z = 2; F(000) = 1264, $\rho_{calcd.}$ = 1.377 g cm^{-3}, μ = 0.786 mm^{-1}, $2\theta_{max}$ = 52.9°. No. of data collected = 34983, no. of unique data = 11756 (R_{int} = 0.075), no. of parameters refined = 744; R_1 = 0.0515 for 10049 observed reflections [$F_o > 4\sigma(F_o)$], ωR_2 = 0.1360 for all data {weighting scheme $w^{-1} = \sigma^2(F_o^2) + (0.0632P)^2 + 4.2517P$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$}, S = 1.085, maximum positive and negative peaks in final difference Fourier map: 1.06 and −1.59 e·Å^{-3}. CCDC-194640 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.uk).

Synthesis of Schiff-Base Ligand L (R = C$_{14}$, R′ = C$_{18}$): 2-Hydroxy-4-tetradecyloxybenzaldehyde was prepared by refluxing 2,4-dihydroxybenzaldehyde (0.1 mol, 13.82 g) with 1-bromotetradecane (0.1 mol, 27.73 g) in DMF for 4 hours, with $KHCO_3$ (0.1 mol, 10.01 g) as the base. After leaving to cool to room temperature, the reaction mixture was poured into an aqueous HCl solution (6 N). The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude aldehyde was purified by crystallisation from hot acetonitrile. Yield: 73% (24.33 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, 3 H, CH_3), 1.02−1.60 (m, 22 H, CH_2), 1.80 (m, 2 H, CH_2−CH_2−O), 4.00 (t, 2 H, CH_2-O), 6.40 (d, 1 H, H-aryl), 9.70 (s, 1 H, CH=O) ppm. J_o = 8.5, J_m = 2.5 Hz.

The Schiff-base ligand was prepared by refluxing 2-hydroxy-4-tetradecyloxybenzaldehyde (0.05 mol, 16.72 g) with *n*-octadecylamine (0.05 mol, 13.45 g) in toluene for 3 hours. A Dean−Stark trap was used to extract the released water and a few drops of glacial acetic acid (catalyst) were added. The solvent was evaporated and the crude product was crystallised from absolute ethanol. Yield: 93% (27.20 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 6 H, CH_3), 1.10−1.50 (m, 52 H, CH_2), 1.67 (m, 2 H, N−CH_2−CH_2), 1.77 (m, 2 H, CH_2−CH_2−O), 3.50 (t, 2 H, N−CH_2), 3.96 (t, 2 H, CH_2−O), 6.32 (dd, 1 H, H-aryl), 6.36 (d, 1 H, H-aryl), 7.06 (d, 1 H, H-aryl), 8.08 (s, 1 H, CH=N), 14.1 (s, 1 H, OH) ppm. J_o = 8.5,

J_m = 2.5 Hz. $C_{39}H_{71}NO_2$ (585.99): calcd. C 79.94, H 12.21, N 2.39; found C 80.05, H 12.12, N 2.17.

Synthesis of [La(dbm)$_3$]: An aqueous solution of $La(NO_3)_3{\cdot}6H_2O$ (0.01 mol, 4.33 g) was added to a solution of dibenzoylmethane (0.01 mol, 2.24 g) in ethanol and 10 mL of $NaOH_{aq}$ (1 M). The mixture was stirred overnight, and then filtered and dried in vacuo. Yield: 85% (6.84 g). $C_{45}H_{33}LaO_6$ (808.7): calcd. C 66.84, H 4.11; found C 67.02, H 4.27.

Synthesis of [La(dbm)$_3$(L)$_2$]: A solution of [La(dbm)$_3$] (3 mmol; 2.42 g) in absolute ethanol was added dropwise to a solution of 2-hydroxy-*N*-octadecyloxy-4-tetradecyloxybenzaldimine (L) (3 mmol; 1.76 g) in absolute ethanol at 50 °C. The adduct precipitated immediately. After the mixture had been stirred overnight at room temperature, the precipitate was filtered off, washed with ethanol and dried in vacuo. The compound was obtained as a pale-yellow powder. Yield: 91% (2.72 g). IR (KBr): $\tilde{\nu}$ = 1654 (C=N, str.), 1552 (C=O, str.) cm^{-1}. $C_{123}H_{175}LaN_2O_{10}$ (1980.6): calcd. C 74.57, H 8.91, N 1.42; found C 74.74, H 8.97, N 1.30.

For further details of yields, elemental analysis and spectral data of the complexes, see Supporting Information (see also the footnote on the first page of this article).

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