

Coordination-Based Symmetric and Asymmetric Bilayers on Gold Surfaces

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This paper is dedicated to the memory of Dr. Jacqueline Libman, whose untimely death was a great loss to her family, to her colleagues, and to science

Abstract: A novel type of bilayer on a gold surface, based upon metal-ion coordination to hydroxamate moieties, is described. Tailor-made bifunctional ligands containing hydroxamate groups (for metal coordination) and a cyclic disulfide residue (for surface attachment) have been prepared. The bishydroxamate binding site forms 2:1 ligand/metal complexes with octacoordinating metal ions such as Zr^{IV}, Ce^{IV}, and Ti^{IV}; the cyclic disulfide moiety anchors the

complex to the gold surface. Two routes to bilayer formation are demonstrated: i) a one-step process from preformed 2:1 complexes, and ii) a stepwise process including formation of the ligand monolayers followed by binding of a guest ion and a second layer of ligand molecules.

Keywords: gold • hydroxamates • layered compounds • self-assembly • transition metals

The former approach allows full characterization of the complexes before bilayer assembly, whereas the latter enables construction of either symmetric (identical) or asymmetric (nonidentical) bilayers. Both types of bilayers were characterized by ellipsometry, contact angle, and XPS measurements. Symmetric bilayers obtained by the two processes have similar properties.

Introduction

Interest in nanomaterials that could provide photoconductors and electrochromic or nonlinear optical elements, as well as electronic analogues, has stimulated extensive research aimed at the generation of functional molecular assemblies.^[1] A prerequisite for the realization of molecule-based functional devices is the development of a methodology for integrating functional molecular components into well-ordered assemblies with a defined supramolecular architecture. Hence, multilayers have been prepared from single-chain molecules with polar head groups by using metal ions as templates or

intercalating agents between adjacent layers. Examples are the use of Zr^{IV},^[2,3] Hf^{IV},^[4] and Al^{III}^[5] in conjunction with phosphoric acids, and Cu^{II}^[6,7] with carboxylic acids.

Here we describe a novel kind of self-assembled organic bilayer, in which chelation of metal ions to pairs of tetradentate ligands provides assemblies whose architecture is dictated by the nature of the metal and the coordinating ligand. As building blocks, we synthesized molecules that integrate a cyclic disulfide group for immobilization onto gold^[8] and two extending chains, each terminated with a hydroxamate functionality. The bishydroxamate obtained is well suited for binding octacoordinating^[9] guest ions such as tetravalent Ti^{IV}, Zr^{IV}, or Ce^{IV}, forming 2:1 ligand/metal complexes with well-defined geometries. In general, complexes with two types of geometry, namely antiprism and dodecahedral, are known. Despite differences in symmetry (and consequently in NMR spectra), both geometries lead to very similar structures that differ mainly in the angle between the metal and the binding ligands.

These systems form bilayers on gold by either of two processes: i) a one-step process, using the preformed 2:1 complexes; ii) a stepwise process involving formation of the ligand monolayers followed by successive binding of the guest ions and a second monolayer of ligand molecules. The one-step approach allows the construction of symmetric^[11] bilayers, while providing the possibility of full characterization of the 2:1 complexes before the bilayer is assembled; this is

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useful in substantiating the bilayer composition. The step-by-step procedure has the advantage of enabling construction of asymmetric (as well as symmetric) bilayers. The similarity in the properties of bilayers prepared by the two methods provides confidence in the structures of these assemblies.

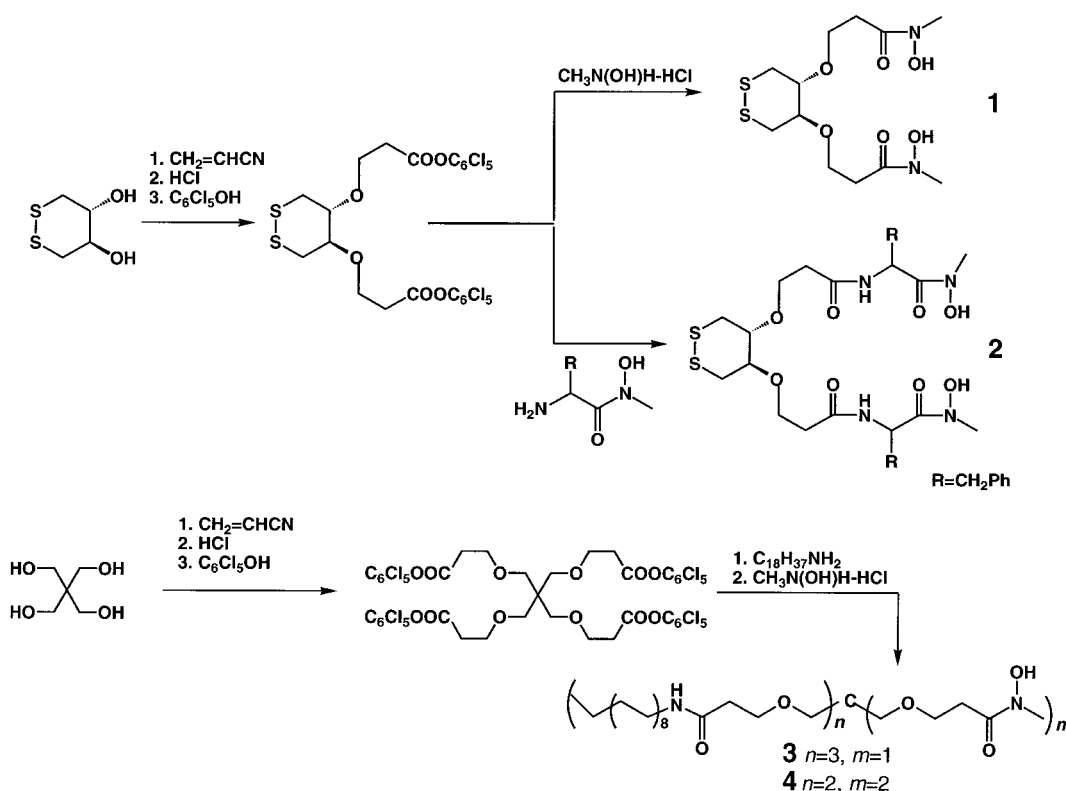
Results and Discussion

Design and synthesis: Tailor-made bifunctional ligands containing hydroxamate groups and a disulfide residue were prepared. The use of the cyclic disulfide as an immobilization group^[10] decreases the number of degrees of freedom of the molecules, resulting in the two extending chains forming a defined cavity and molecular envelope. It also helps in maintaining the cavity properties upon possible S–S bond cleavage during self-assembly. The formation of intramolecular complexes on the surface is therefore preferred to intermolecular complex formation, although the latter cannot be ruled out. The lability of the metals provides various possibilities as discussed below.

The ligands **1**, **2**, **3**, and **4** were synthesized in two main steps (Scheme 1): i) preparation of the activated anchors (the diphenolates and tetraphenolates); and ii) coupling of the anchors with the chosen nucleophiles. The symmetric metal complexes of 2:1 ligand:metal stoichiometry were prepared by mixing ligand **1** with [Ce(acac)₄] or [Zr(acac)₄] in CHCl₃, or by heating with [Ti(isopropoxide)₄] in benzene.^[9a] The structures of all the ligands and complexes were confirmed by a combination of FAB-MS, IR, and ¹H NMR spectroscopy.

Preformed bilayer assemblies: In the one-step process, symmetric bilayers of **1** with Zr^{IV}, Ce^{IV}, and Ti^{IV} were assembled by immersion of gold substrates in solutions of the preformed complexes (Scheme 2), and characterized by ellipsometry, contact angle (CA) measurements, XPS and ac-impedance spectroscopy (Table 1). A thickness of 11–14 Å was determined ellipsometrically for all the bilayers.^[12] This is lower than the theoretical thickness (16–17 Å) calculated from models with the assumption of perpendicular orientation, and probably indicates a tilt from the surface normal rather than incomplete coverage, because these bilayers have high coverage values (Table 1). The water CAs of the bilayers are rather low, with a relatively large CA hysteresis. This is likely to result from the distal position of the disulfide groups, which is dictated by the bulky nature of the metal-binding center.

The chemical composition of the bilayers was confirmed by XPS measurements^[14] (Table 1). The N/S atomic concentration ratio (0.97–1.26:1) is close to the relative concentration ratio of 1:1 in the bilayers. The S/metal ion ratio (4.2–6.8:1) is also close to the expected ratio (4:1); in this case the difference evidently arises from the fact that two sulfur atoms are located in the outermost part of the layer so that their intensity is enhanced compared with that of the metal ion, which is located in the center of the molecular structure. Another source of the differences between observed and theoretical ratios is the relatively large error in integrating the very small metal-ion signal (for Table 1 a minimum value was taken). The carbon concentration is larger than expected relative to all other elements. This discrepancy might be attributable to hydrocarbon impurities physically adsorbed on the bilayers. An excess of oxygen is also observed, which

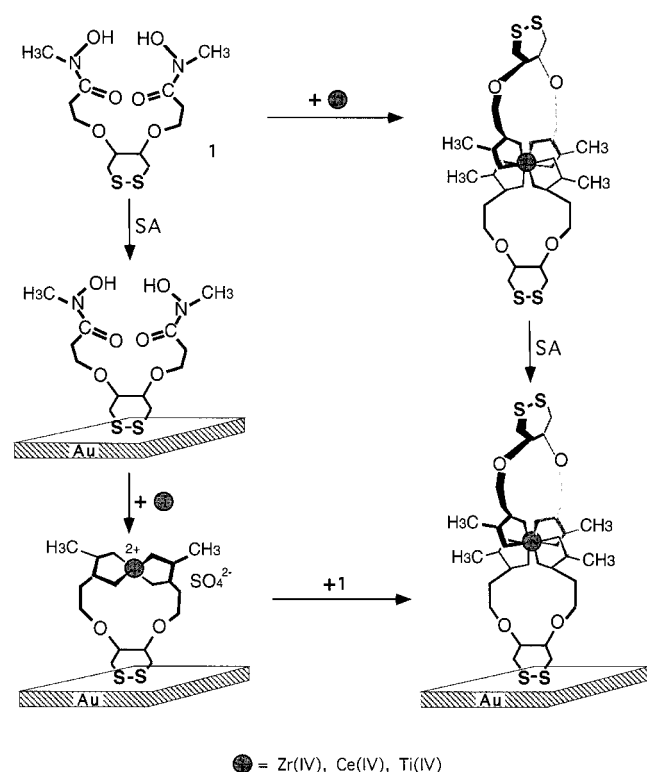


Scheme 1. Preparation of: **1**, a racemic mixture of bis-hydroxamate binder with disulfide anchor; **2**, a diastereomeric mixture of bis-hydroxamate binder containing an amino acid and disulfide anchor; **3**, a monohydroxamate trioctadecyl binder; **4**, a bis-hydroxamate dioctadecyl binder.

Table 1. Ellipsometric thickness, advancing (Adv) and receding (Rec) contact angles (CAs), surface coverage, and XPS results for symmetric and asymmetric bilayers, assembled either from preformed complexes or by stepwise construction (see text). Ellipsometric thicknesses were calculated using $n_f = 1.45 - 1.65$.

Bilayer	Theoretical perpendicular thickness (Å) ^[a]	Ellipsometric thickness (Å)	Adv CA (H ₂ O)	Rec CA (H ₂ O)	% Coverage ^[b]	XPS results (atom %)							
						Au 84 eV	S 162 eV	C 285 eV	O 532 eV	N 400 eV	Zr 182 eV	Ce 884 eV	Ti 459 eV
Assembled from preformed complexes													
1-Zr-1	16-17	11-14	51	31	96	31.7	3.4	48.1	13	3.3	0.5	-	-
1-Ce-1	16-17	11-14	58	25	87	35.4	2.5	45.6	13	3.1	-	0.6	-
1-Ti-1	16-17	11-14	50	28	96	43.1	2.3	34.2	17	2.9	-	-	0.5
Assembled by stepwise construction													
1-Ce-1	16-17	13-16	57	25	95	36.0	4.4	40	15	3.4	-	0.8	-
1-Ce-2	18-20	12-15	61	27	96	48.1	3.1	33.3	11.8	3.4	-	0.3	-
1-Ce-3	40	32-34	70	39	71	35.1	1.5	45.7	14.9	2.3	-	0.8	-
1-Ce-4	40	21-26	72	45	82	36.7	2.5	44.3	12.3	3.8	-	0.8	-

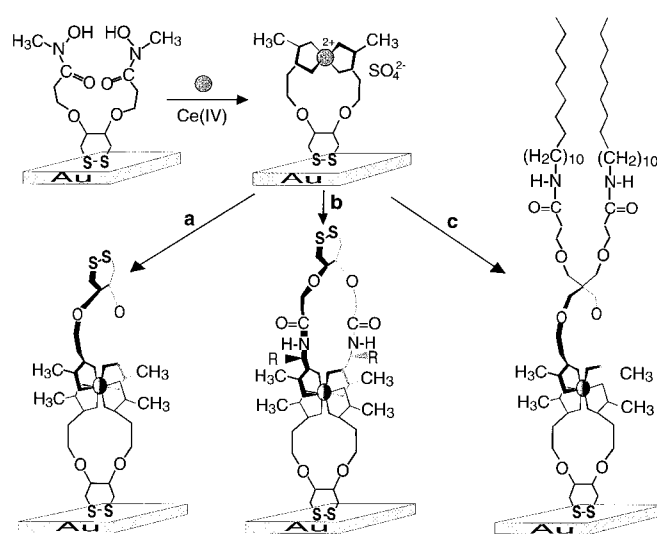
[a] Assuming a perpendicular orientation. [b] From ac-impedance measurements^[16] with $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{Fe}^{3+/2+}$ and $\text{Fe}(\text{CN})_6^{3-/4-}$.



Scheme 2. Formation of symmetric bilayers on a gold surface using either a preformed complex or a stepwise procedure. Binding of the bishydroxamate ligand to the tetravalent ion involves loss of two protons from the OH groups.

might be due to some gold oxide remaining on the surface^[15] or to air contaminants, water molecules incorporated in the layer, or other similar causes. The extent of surface coverage determined by ac-impedance spectroscopy^[16] is rather high, in the range from 87% to 96%.

Stepwise bilayer assemblies: Stepwise formation of symmetric and asymmetric bilayers was carried out with Ce^{IV} salts. The bilayer formation, shown schematically in Scheme 3, involves i) adsorption of the disulfide dihydroxamate **1** on Au to obtain a ligand monolayer (ellipsometric thickness 9 Å for $n_f = 1.45$);



Scheme 3. Stepwise formation of symmetric (route a) and asymmetric (routes b, c) bilayers on a gold surface.

ii) exposure of the monolayer to aqueous solutions of $\text{Ce}(\text{SO}_4)_2$ or $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$ followed by rinsing in water, to provide the respective monolayer complex (ellipsometric thickness 9–12 Å for $n_f = 1.45 - 1.65$); and iii) exposure of the monolayer complex to solutions of **1** to obtain a symmetric bilayer (route a), or to solutions of **2-4** to obtain asymmetric bilayers (routes b, c) (ellipsometric thicknesses are summarized in Table 1). The asymmetric bilayers containing fatty acids, **1-Ce-3** and **1-Ce-4**, were constructed in order to establish the existence of a bilayer by means of CAs, ellipsometry, and FTIR (see below).

Table 1 summarizes the properties of symmetric and asymmetric bilayers formed by the stepwise procedure. The similarity of the symmetric Ce^{IV} -based bilayers to those derived from the preformed complexes indicates that the bilayer structures of the assemblies formed by the two methods are similar. XPS measurements confirmed the chemical composition of the bilayer^[17] and showed the respective metal ions and relative atomic concentrations, as discussed above. The relative concentration of sulfur (compared with all other elements, excluding the metal) in bilayers

of **1**–Ce–**3** and **1**–Ce–**4** is smaller than in bilayers of **1**–Ce–**1** and **1**–Ce–**2**. This is attributable to the higher carbon and oxygen concentrations in ligands **3** and **4**, and to the greater thickness of the layer above the sulfur atoms, which reduces the escape probability of the S photoelectron. In **1**–Ce–**1** and **1**–Ce–**2** bilayers, two of the sulfur atoms are located in the outermost part of the film and their signal intensity is therefore enhanced.

FTIR results confirm the presence of the hydrocarbon chains in bilayers containing **3** and **4** as the second layer, by the appearance of methylene stretching peaks at 2925 and 2857 cm^{-1} following binding of **3** or **4** to the complex monolayer. This is seen readily in Figure 1 for a bilayer of **2**–Ce–**3** in comparison with a monolayer of **2**. For bilayers containing **1** or **2** as the second layer the increase in the methylene peaks is too small to be detected.

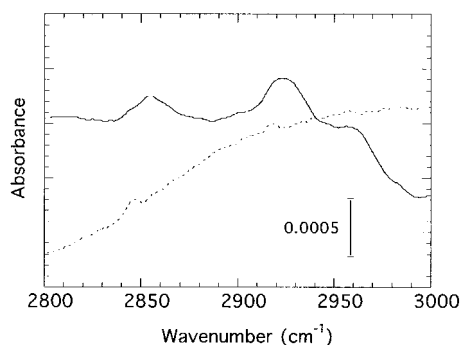


Figure 1. FTIR spectra of a bilayer of **2**–Ce–**3** (unbroken line) and a monolayer of **2** (broken line).

The ellipsometric thicknesses of **1**–Ce–**3** and **1**–Ce–**4** (32–34 Å and 21–26 Å, respectively) are, as expected, larger than those of the other bilayers (12–16 Å), but lower than the 40 Å calculated theoretically for fully extended chains. This is attributed to disorder of the hydrocarbon chains, resulting from the large area per molecule (approximately 60 Å², calculated for the cross-section of the complex), which prevents dense packing of the chains. The disorder would be greater with the **1**–Ce–**4** bilayer, which contains two hydrocarbon chains per molecule, than with the **1**–Ce–**3** bilayer, which possesses three hydrocarbon chains, as the measured thicknesses show.

The water CAs are consistent with the surface modification process. The advancing CAs decrease from 50° on the ligand monolayer to 45° on the complexed monolayer. This may be a result of the greater hydrophilicity of the surface provided by the metal ion and its counterions. Upon introduction of the second organic layer the CAs increase (Table 1), indicating the increase in hydrophobicity. The latter is particularly noticeable when the second organic layer comprises long hydrocarbon chains (ligands **3** and **4**), in which case the CA values reach 70–72°.

The lability of the metal ions used for bilayer formation provides the possibility of facile exchange of the outer layer. This unusual property was demonstrated by i) construction of a bilayer of **1**–Zr–**1**; ii) removal of the second layer upon decomposition of the complex (30 min in 0.1M HCl); and iii)

reconstruction of the bilayer by immersion in Zr⁴⁺ followed by **1**, to obtain the **1**–Zr–**1** bilayer. In a typical experiment the variation in the ellipsometric thickness from 14–18 Å to 9–11 Å to 16–20 Å during the three stages described above^[18] demonstrated how the outer layer in the bilayer structure could be manipulated.

Conclusion

The present study introduces a general and convenient route for the preparation of geometrically defined symmetric as well as asymmetric bilayers on solid substrates. The approach relies on the preparation of supramolecular building blocks that integrate metal-ion binding sites and surface anchoring groups in a single molecule. Selection of metal ions with defined coordination geometries (in the present case, the closely related antiprism and dodecahedron) makes it possible to generate the desired assemblies. This method is highly versatile as it allows convenient tuning of the binding groups, the anchoring residue, and the bridges between the two; it also facilitates manipulation of the bilayers already formed, because of the labile nature of the metal ions used.

The method can be extended to the formation of chiral bilayers, and may be useful as a general route for binding chosen functional groups to surfaces. Moreover, preliminary results have indicated the possibility of extending this technique to the formation of organized multilayers, by using tetrahydroxamates as bifunctional linkers in a stepwise assembly procedure.^[19] These aspects are being investigated further.

Experimental Section

Chemicals: Chloroform (Biolab, AR), was passed through a column of activated basic alumina (Alumina B, Akt. 1, ICN). Ethanol (Merck, AR), H₂O₂ (Merck), NaOH (Merck, AR), HNO₃ (Palacid, 69–70%), HCl (Frutarom, 32%), Na₂SO₄ (Merck, AR), K₄[Fe(CN)₆] (Fluka, AR), K₃[Fe(CN)₆] (Fluka, AR), KCl (Merck, AR), [Ru(NH₃)₆Cl₃] (Strem), Fe₂(SO₄)₃ (Fluka, AR), FeSO₄, Ce(SO₄)₂ (BDH, AR), [(NH₄)₂Ce(NO₃)₆] (BDH, AR), ZrCl₄ (Merck, AR) were used as received. Gases used were argon (99.996%), oxygen (99.5%), nitrogen (99.999%), and dry purified air. Water was triply distilled.

Gold electrodes: Gold films 1000 Å thick were evaporated onto optically-polished n-type single-crystal (111) silicon wafers (Aurel, Landsberg, Germany), cut into approximately 22 × 11 mm slides, as previously described.^[20] The gold-covered slides were annealed in air for 3 h at 250 °C and left to cool to ambient temperature.^[20]

Monolayer preparation: The gold substrates were pretreated in mild oxygen plasma, then rinsed in ethanol.^[20] In some cases O₂ plasma was replaced with UV/ozone treatment by means of a UVOCS instrument. Monolayers were adsorbed by immersion of gold substrates in 3 mm solutions of **1** or **2** in EtOH/CHCl₃ (2:1, v/v) for 17–24 h. The slides were rinsed successively with dry chloroform and absolute ethanol, then immersed in ethanol for 20 min and dried under a stream of purified air.

Preparation of preformed bilayers: Preformed bilayers were assembled by the procedure described above for the monolayers.

Step-by-step preparation of bilayers: Following monolayer preparation (as above), the slides were immersed in aqueous solutions containing the tetravalent ions Ce⁴⁺ or Zr⁴⁺ (1–5 mM Ce(SO₄)₂, [(NH₄)₂Ce(NO₃)₆], or ZrCl₄). After 15 min in the ionic solution the slides were washed for 15 min in a mixture of 70% EtOH/30% H₂O, then immersed overnight in a 3 mM

solution of the molecules needed to form the second organic layer, either in EtOH/CHCl₃ (2:1, v/v) (**1**, **2**) or in CHCl₃ (**3**, **4**). The slides were rinsed with chloroform, then ethanol.

Ellipsometry: A Rudolph Research Auto-EL IV null ellipsometer operating at an angle of incidence of 70° and a wavelength of 632.8 nm was used for ellipsometric measurements according to the previously described procedure.^[20]

Contact angle (CA) measurements: Water CAs were measured as previously described,^[20] at an accuracy of ±2°. (The two commonly used organic solvents, bicyclohexyl and hexadecane, wetted the monolayers completely.)

Ac-impedance spectroscopy: Ac-impedance measurements were performed in a conventional three-electrode cell with either a saturated calomel (SCE) or a mercurous sulfate (MSE) reference electrode and a platinum disk counter-electrode. The instrumentation and procedure have been described previously.^[20] The coverage was measured with three different redox couples: i) 5 mM Fe²⁺ + 5 mM Fe³⁺ + 0.2 M Na₂SO₄ (using MSE); ii) 5 mM Fe(CN)₆³⁻ + 5 mM Fe(CN)₆⁴⁻ + 0.5 M KCl (using SCE); iii) 0.5 mM Ru(NH₃)₆³⁺ + 0.5 mM Ru(NH₃)₆²⁺ + 0.2 M Na₂SO₄ (using MSE). The Ru(NH₃)₆^{3+/2+} solution was prepared by dissolving 1.0 mM Ru(NH₃)₆³⁺ in aqueous 0.2 M Na₂SO₄; equimolar concentrations of Ru(NH₃)₆²⁺ and Ru(NH₃)₆³⁺ were achieved by partial galvanostatic reduction of Ru(NH₃)₆³⁺ until the potential of a Pt electrode immersed in the solution reached the half-wave potential of the Ru(NH₃)₆^{2+/3+} couple. The working electrode for the electrolysis was a Pt gauze. The counter-electrode was a Pt wire, separated from the bulk of the solution by a porous glass membrane.

X-Ray photoelectron spectroscopy (XPS): XPS measurements were carried out with an Axis HS Kratos XPS system and a monochromated Al_{Kα} X-ray source (*hν* = 1486.6 eV). All XPS data were acquired at a normal takeoff angle.

FTIR spectroscopy: FTIR spectra were obtained with a nitrogen-purged Bruker IFS66 FTIR spectrometer operating in the reflection mode with the incident beam at an angle of 80°, focused on the sample with an *f*/4.5 lens. The mercury/cadmium telluride (MCT) detector was cooled by liquid nitrogen. The resolution of the spectra was 2 cm⁻¹. The instrument was programmed to run 50 scans with the reference (thiophenol-coated gold substrate) and then 50 scans with the sample, and to collect 80 such cycles.

Preparation of dipentachlorophenolate: *trans*-1,2-Dithiane-4,5-diol (3.50 g; 22.9 mmol) was dissolved in dry acrylonitrile (3.33 mL; 50.5 mmol), cooled to 0 °C, treated with 40% NaOH (120 μL), and stirred overnight at room temperature (RT). Neutralization of the reaction mixture with 1N HCl (300 mL) and extraction with ethyl acetate provided the dicyano derivative. The latter (6.17 g; 24 mmol) was hydrolyzed by heating at 95–100 °C for 2 h with concentrated HCl (5.46 mL; 48.0 mmol), and the diacid obtained (6.06 g; 20.0 mmol) was converted to the dipentachlorophenolate by reaction with dimethylaminopyridine (DMAP, 0.25 g; 2.00 mmol), pentachlorophenol (11.9 g; 45.0 mmol), and *N,N'*-diisopropylcarbodiimide (9.5 mL; 60 mmol) in acetonitrile overnight. Chromatographic purification provided the active ester in 14% yield. M.p. 118–120 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 4.02 (t, 2H, OCH₂), 3.42 (m, 1H, CHO), 3.18 (ABq, ³J = 13.4 Hz, 1H, SCH), 2.93 (m, 3H, CH₂CO and SCH); IR (CDCl₃): ν = 1781 (COOC₆Cl₅), 1108 cm⁻¹ (OCH₂).

Preparation of dimethylhydroxamate 1: Dipentachlorophenolate (1.1 g; 1.4 mmol) was treated with a suspension of methylhydroxylamine hydrochloride (0.36 g; 4.2 mmol) and triethylamine (0.6 mL; 4.2 mmol) in dry CHCl₃ and was stirred overnight at RT. Chromatographic purification provided **1** as an oily material in 55% yield. ¹H NMR (400 MHz, MeOD, 25 °C): δ = 3.86 (m, 2H, OCH₂), 3.37 (m, 1H, CHO), 3.19 (s, 3H, CH₃), 3.21 (m, 1H, SCH), 2.76 (m, 3H, SCH and CH₂CO); IR (CDCl₃): ν = 3300 (NOH, NH), 1639 cm⁻¹ (CONOH); DCI MS (NH₃): *m/z* = 355.2 [(*M*+H)⁺], 372.2 [(*M*+NH₄)⁺].

Preparation of Ce^{IV} and Zr^{IV} 1:2 metal/ligand complexes of 1: Solutions of **1** (10%_{w/w}) in dry CHCl₃ were treated with 0.5 equiv of [Ce(acac)₃] or [Zr(acac)₄] overnight under argon and concentrated to dryness. The crude material was dissolved in a minimum volume of CH₂Cl₂ and the product was precipitated by addition of hexane. **1-Zr-1**: ¹H NMR (400 MHz; CDCl₃; 25 °C): δ = 3.97 (m, 2H, OCH_A and OCH_B), 3.70 (m, 2H, OCH_A and OCH_B), 3.46 (s, 3H, NCH₃), 3.42 (s, 3H, NCH₃), 3.31 (ABq, 1H, CH_BO), 3.19 (ABq, 1H, CH_AO), 3.12 (t, 1H, SCH_B), 3.08 (t, 1H, SCH_A), 2.84 (m, 2H, SCH_A and SCH_B), 2.60 (dt, 2H, CH_ACO and CH_BCO), 2.44

(dt, 2H, CH_ACO and CH_BCO); IR (CDCl₃): ν = 1623 cm⁻¹ (CON), ES MS: *m/z* = 795.58 [*M*+H]⁺. **1-Ce-1**: ¹H NMR (400 MHz; CDCl₃; 25 °C): δ = 4.03 (dABq, 2H, OCH_A and OCH_B), 3.75 (ABq, 1H, OCH_B), 3.71 (ABq, 1H, OCH_A), 3.43 (s, 3H, NCH₃), 3.39 (s, 3H, NCH₃), 3.33 (ABq, 1H, CHO), 3.26 (ABq, 1H, CHO), 3.14 (dd, ³J = 2.92 Hz, ³J = 13.5 Hz, 2H, SCH_A and SCH_B), 2.84 (dd, ³J = 3.0 Hz, *J* = 12.8 Hz, 2H, SCH_A and SCH_B), 2.67 (dABq, 2H, CH_ACO and CH_BCO), 2.39 (ABq, ³J = 3.3 Hz, *J*_{AB} = 15.2 Hz, 1H, CH_BCO), 2.36 (ABq, ³J = 2.81 Hz, *J*_{AB} = 14.7 Hz, 1H, CH_ACO); IR (CDCl₃): ν = 1601 cm⁻¹ (CON); ES MS: *m/z* = 844.91 [*M*+H]⁺.

Preparation of Ti^{IV} 1:2 metal/ligand complexes of 1: Heating of dihydroxamate **1** with 0.5 equiv of [Ti(isopropoxide)₄] in benzene in a Dean–Stark apparatus according to a literature procedure for monohydroxamates^[9a] provided the desired complex, which was purified by precipitation from CH₂Cl₂/hexane. ¹H NMR (270 MHz; CDCl₃; 25 °C): δ = 3.71 (m, 2H, OCH_A and OCH_B), 3.58 (m, 2H, OCH_A and OCH_B), 3.34 (s, 3H, NCH₃), 3.32 (s, 3H, NCH₃), 3.08 (m, 2H, CH_AO and CH_BO), 3.08 (m, 2H, SCH_A and SCH_B), 2.50 (m, 2H, SCH_A and SCH_B), 2.12 (m, 4H, CH₂CO and CH₂CO); IR (CDCl₃): ν = 1601 cm⁻¹ (CON); DCI MS (butane): *m/z* = 355 [(*M*+H)⁺] (metal-free ligand **1**).

Preparation of bishydroxamate 2: Treatment of dipentachlorophenolate (100 mg; 0.13 mmol) with NH₂CHBnCONHMe^[21] (60 mg; 0.38 mmol) in dry CHCl₃ overnight at RT and chromatographic purification provided a diastereomeric mixture of the dihydroxamates **2** (60% yield). M.p.: 88–90 °C; ¹H NMR (400 MHz; CDCl₃, 25 °C, TMS): δ = 10.3 (s, 1H, NOH), 9.9 (s, 1H, NOH), 8.2 (br, 1H, NH), 7.37 (d, ³J = 7.3 Hz, 1H, NH), 7.28 (m, 10H, Ph), 5.32 (m, 2H, CH^α), 3.78 (m, 1H, OCH), 3.69 (m, 2H, OCH and OCH), 3.46 (m, 1H, OCH), 3.29 (s, 3H, NCH₃), 3.23 (m, 1H, CHO) 3.22 (s, 3H, NCH₃), 3.17 (d, ³J = 6.1 Hz, 2H, CH₂Ph), 3.13 (ABq, 1H, CHO), 3.02 (m, 4H, SCH₂ and CH₂Ph), 2.80 (m, 2H, SCH₂), 2.41 (t, 2H, CH₂CO), 2.26 (t, 1H, CHCO), 2.22 (t, 1H, CHCO); IR (CDCl₃): ν = 3300 (NOH, NH), 1632 cm⁻¹ (CON). In order to characterize each of the isomers unambiguously, a sample was separated by formation of its Cu^{II} complexes and the free ligands were regenerated.

Preparation of fatty-acid (octadecyl) derivatives 3 and 4: A mixture of tetraphenolate^[22] with octadecylamine (3 or 2 equiv to obtain **3** or **4**, respectively) in dry chloroform was stirred overnight in the presence of hydroxysuccinimide (0.1 equiv). The fatty-acid derivatives were purified by chromatography and each was treated with a suspension of methylhydroxylamine hydrochloride (1 or 2 equiv to obtain **3** or **4**, respectively) and Et₃N in chloroform overnight. Purification by chromatography provided **3** or **4** respectively as oils. **3**: ¹H NMR of (400 MHz, CDCl₃, 25 °C): δ = 3.71 (t, 2H, -CH₂O), 3.65 (t, ³J = 5.7 Hz, 6H, CH₂O), 3.29 (s, 3H, CH₃), 3.27 (br, 2H, OCH₂), 3.23 (ABq, ³J = 6.8 Hz, *J*_{AB} = 13 Hz, 6H, OCH_AH_B), 2.74 (t, 2H, CH₂CO), 2.40 (t, ³J = 5.7 Hz, 6H, CH₂CO), 1.50 (t, ³J = 6.5 Hz, 6H, NHCH₂), 1.25 (br, 96H, aliphatic chain), 0.87 (t, ³J = 6.9 Hz, 9H, CH₃); IR (CDCl₃): ν = 1654 cm⁻¹ (C=O); FAB MS: *m/z* = 1208 [(*M*+H)⁺]. **4**: ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 3.71 (t, 2H, CH₂O), 3.64 (t, ³J = 5.4 Hz, 2H, CH₂O), 3.3 (s, 3H, CH₃), 3.28 (br, 2H, OCH₂), 3.22 (ABq, ³J = 6.4 Hz, *J*_{AB} = 12.8 Hz, 2H, OCH_AH_B), 2.75 (t, 2H, CH₂CO), 2.39 (t, ³J = 5.6 Hz, 2H, CH₂CO), 1.56 (t, ³J = 5.6 Hz, 2H, CONHCH₂), 1.25 (br, 32H, aliphatic chain), 0.86 (t, ³J = 6.8 Hz, 3H, CH₃); IR (CDCl₃): ν = 1656 cm⁻¹ (CON); FAB MS: *m/z* = 985 [(*M*+H)⁺].

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