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Synthesis and Crystal Structure Investigations of Trivalent Rare Earth (Y^{3+}, Nd^{3+}, Er^{3+}) Thienyl-Substituted Methoxides

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The synthesis and structural characterization of rare earth alkoxides with thiophene-based substituents are presented. Monomeric metal thienylmethoxides have been prepared by aminolysis reactions between $M[N(SiMe_3)_2]_3$ (M = Y^{3+}, Nd^{3+}, Er^{3+}) and the structurally characterized tertiary alcohols HO–$C(C_4H_3S)_3$ (**1**) or HO–$C(C_8H_5S_2)_3$ (**2**). The metal alkoxide derivatives of these thiophene-substituted alcohols have been isolated as air-sensitive base adducts, their molecular structures being investigated by single-crystal X-ray crystallography. The coordination spheres around the metal centres are distorted trigonal-bipyramidal for the yttrium thienylmethoxides $Y[OC(C_4H_3S)_3]_3(thf)_2$ (**3a**), {$Y[OC(C_4H_3S)_3]_3(thf)_2$}·toluene (**3b**), $Y[OC(C_4H_3S)_3]_3(py)_2$ (**4a**), {$Y[OC(C_4H_3S)_3]_3(py)_2$}·toluene (**4b**) and $Y[OC(C_8H_5S_2)_3]_3(thf)_2$ (**5**). An almost tetrahedral geometry has been detected for $Er[OC(C_8H_5S_2)_3]_3(thf)$ (**9**), whereas an approximately octahedral geometry was found for {$Nd[OC(C_4H_3S)_3]_3(thf)_3$}·thf (**6**), {$Nd[OC(C_8H_5S_2)_3]_3(thf)_3$}·4thf (**7**) and $Er[OC(C_4H_3S)_3]_3(thf)_3$ (**8**).

Introduction

During the last decade, rare earth chemistry has received much attention, which notably concentrated on derivatives of yttrium and lanthanides. This type of compound has found a variety of applications in catalysis,[1–6] ceramics and electronic materials.[7,8] Lanthanide derivatives are frequently screened to form precursors for MOCVD and for emitting layers in polymer-based light-emitting diodes[9,10] Recently, europium(3+) and terbium(3+) compounds containing thiophenyl-derivatized nitrobenzoic acid[9] and 2-nitro-4-(thiophen-3-yl)benzoic acid[11] ligands were reported. In general, thiophene derivatives are attractive as organic ligands because of the simple formation of polymer films by voltammetric methods.[12–15] Recent studies performed by us on thiophene-functionalized tertiary alcohols have shown that these molecules are good precursors for films generated by electropolymerization and subsequent adhesion of nanoparticles.[16] It seemed therefore promising to probe whether this kind of thiophene-functionalized alcohols could be used to prepare electrochemically active alkoxido ligands in lanthanide coordination chemistry. We report here on the preparation and the structural characterization of rare earth compounds containing this type of thienylalkoxido ligands.

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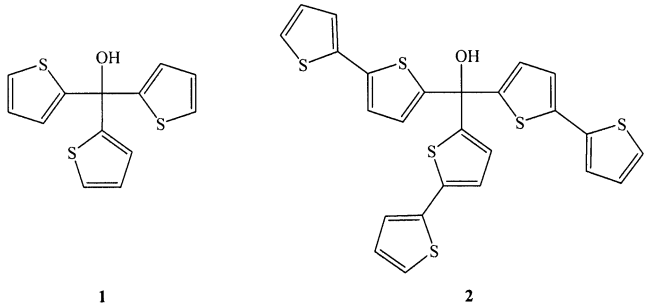
Results and Discussions

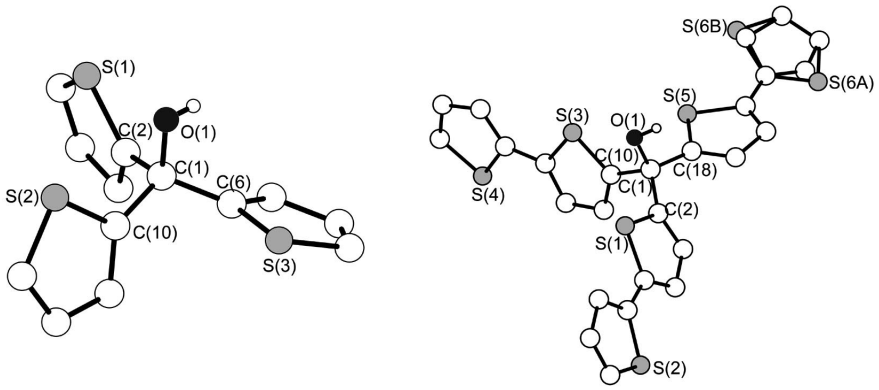
Synthesis of the Ligands

The star-shaped carbinol derivatives tris(2-thienyl)methanol (**1**) and tris(2,2′-bithienyl-5-yl)methanol (**2**) (Scheme 1) were synthesized by following the procedure described.[12,17] They were obtained by a classical nucleophilic addition of three equivalents of (2-thienyl)lithium or 2,2′-bithienyl-5-yllithium, respectively, to ethyl chloroformate. These organic compounds were characterized by ^1H NMR, ^{13}C NMR, IR and elemental analysis. Furthermore, their molecular struc-



1 2

Scheme 1. Star-shaped carbinols **1** and **2**.



1 **2**

Figure 1. Molecular structures of tris(2-thienyl)methanol (**1**) and tris(2,2′-bithienyl-5-yl)methanol (**2**) omitting the hydrogen atoms on carbon atoms. The sulfur atom S(6) in compound **2** is found in two split positions [S(6A) and S(6B)].

tures were determined by X-ray structure analysis for the first time, and the results confirmed the structures proposed in previous works.[12,17]

Colourless crystals of HO–C(C_4H_3S)$_3$ (**1**) and HO–C($C_8H_5S_2$)$_3$ (**2**) were grown at room temperature from hexane[17] or dichloromethane/petroleum ether (3:2), respectively. The results of the structure determination are presented in Figure 1; selected bond lengths and angles are given in Table 1. The geometry around the tertiary carbon centre C(1) is distorted tetrahedral. Due to the packing effect, weak intramolecular interactions between the hydroxy group and the hydrogen atom in the γ position of the thienyl units [2.866(2) Å] for **1** or in the β position of the bithienyl units [2.730(9) Å] for **2** are observed.

Table 1. Selected bond lengths [Å] and angles [°] for **1** and **2**.

1		**2**	
O(1)–C(1)	1.440(4)	O(1)–C(1)	1.440(8)
C(1)–C(2)	1.534(5)	C(1)–C(2)	1.511(10)
C(1)–C(10)	1.523(5)	C(1)–C(10)	1.550(10)
C(1)–C(6)	1.514(5)	C(1)–C(18)	1.509(10)
O(1)–H(4)	2.866(2)	O(1)–H(19)	2.730(9)
O(1)–C(1)–C(6)	110.6(3)	O(1)–C(1)–C(10)	104.7(5)
O(1)–C(1)–C(2)	108.4(3)	O(1)–C(1)–C(2)	109.3(5)
O(1)–C(1)–C(10)	104.9(3)	O(1)–C(1)–C(18)	109.8(5)
C(6)–C(1)–C(10)	113.2(3)	C(18)–C(1)–C(2)	113.6(6)
C(10)–C(1)–C(2)	108.3(3)	C(18)–C(1)–C(10)	111.1(6)
C(6)–C(1)–C(2)	111.2(3)	C(2)–C(1)–C(10)	107.9(5)

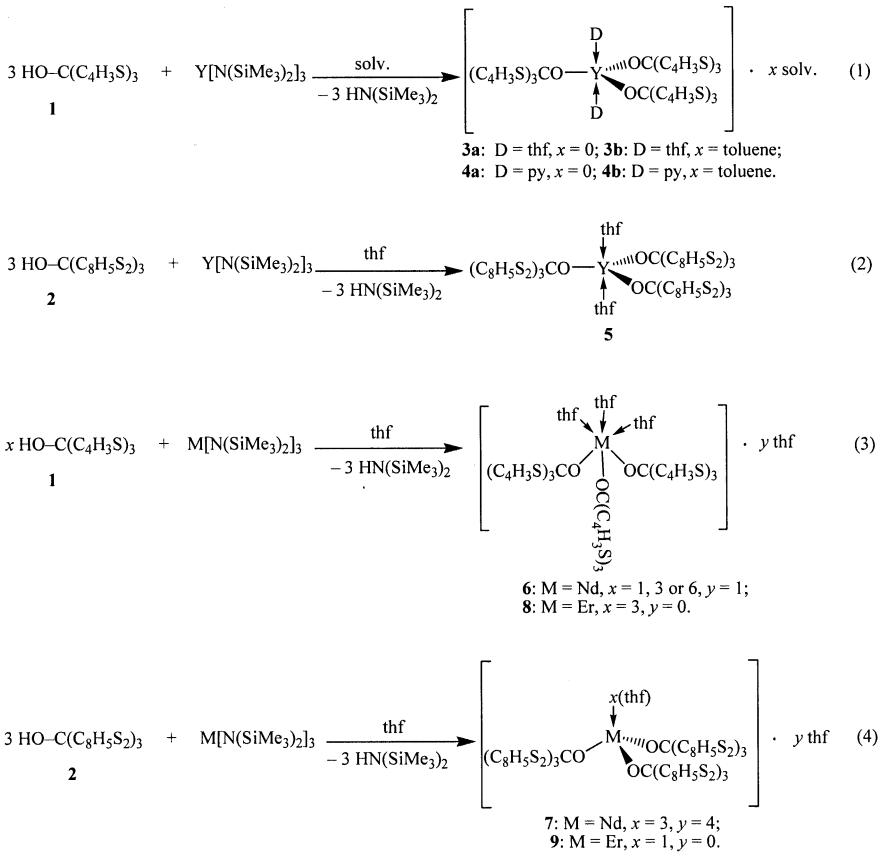
Synthesis of the Rare Earth Thienylmethoxides

To correlate structural and steric effects on the molecular geometry, a series of rare earth thienylmethoxides was prepared. They were synthesized by varying two parameters: (i) the nature of the thienylalkoxido ligand and (ii) the nature of the metal centre. Several synthetic pathways leading to alkoxides have been investigated in the past, such as salt metathesis reactions between MCl_3 and carbinolates[18–21] or aminolysis reactions between M[N($SiMe_3$)$_2$]$_3$ and acidic carbinol[22,23] The latter method has already enabled the preparation of some mono- and dinuclear rare earth alkoxides,[23b,24] the high solubility of silylamides facilitating the isolation of the products. Moreover, the propensity of **1** and **2** to yield alkoxido ligands by covalent M–O bonding is due to their ability to be easily deprotonated in the presence of a silylamide group acting as a base, thus liberating the volatile hexamethyldisilazane. Using this route, the desired compounds were obtained by the smooth reaction between M[N($SiMe_3$)$_2$]$_3$ (M = Y^{3+}, Nd^{3+}, Er^{3+}), which are prepared by following a known procedure,[25] and stoichiometric amounts of **1** or **2** in coordinating solvents such as tetrahydrofuran and pyridine. A summary of the performed syntheses is presented in Scheme 2.

Yttrium Thienylmethoxides

Y[OC(C_4H_3S)$_3$]$_3$(thf)$_2$ (**3a**) and {Y[OC(C_4H_3S)$_3$]$_3$(thf)$_2$}·toluene (**3b**) were synthesized by the reaction between one equivalent of silyl amide {Y[N($SiMe_3$)$_2$]$_3$} and three equivalents of tris(2-thienyl)methanol (**1**) in tetrahydrofuran for two days at room temperature [Scheme 2, Equation (1)]. After evaporation of the solvent, the light-brown solids were redissolved in toluene to obtain colourless single crystals of the yttrium thienylmethoxides (yields: 23% for **3a** and 37% for **3b**). The pyridine adducts Y[OC(C_4H_3S)$_3$]$_3$(py)$_2$ (**4a**) and {Y[OC(C_4H_3S)$_3$]$_3$(py)$_2$}·toluene (**4b**) were prepared in an analogous manner by using a toluene/pyridine solvent mixture in the ratio (9:1) instead of tetrahydrofuran [Scheme 2, Equation (1)]. They could be isolated as light-brown crystals in yields of 10% and 61%, respectively. All these compounds are quite air-sensitive.

The ^{1}H NMR spectrum of **3a** recorded in C_6D_6 displays three broad signals in the integral ratio 9:9:9 attributed to the protons of the thienyl units (δ = 7.10, 6.9 and 6.7 ppm) and two signals due to the methylene protons of the ligated tetrahydrofuran molecules (δ = 3.7 and 1.4 ppm). The broadening of the signals could be due to a dynamic phenomenon of the organic ligands. The ^{1}H NMR spectrum of **3b**, which is also poorly resolved, displays three doublets of



Scheme 2. Routes leading to rare earth alkoxides with thienyl substituents.

doublets due to the protons of the thienyl units in the integral ratio 9:9:9 (δ = 7.1, 6.9 and 6.7 ppm) together with the signals from the protons of the coordinated tetrahydrofuran (δ = 3.7 and 1.4 ppm) and the toluene lattice molecule (δ = 7.0 and 2.5 ppm). The ^{1}H NMR spectrum of **4a** consists of three well-resolved doublets of doublets in the integral ratio 9:9:9 (δ = 6.9, 6.8 and 6.6 ppm) and the protons of pyridine signals (δ = 8.4, 6.9 and 6.6 ppm). Similarly, the ^{1}H NMR spectrum of **4b** displays three doublets of doublets in the integral ratio 9:9:9 attributed to the protons of the thienyl units (δ = 6.9, 6.8 and 6.6 ppm), the protons of pyridine (δ = 8.4, 6.9 and 6.6 ppm) and the methyl protons of the toluene lattice molecule (δ = 7.0 and 2.1 ppm). No dynamic phenomenon is noted in the case of **4**.

A procedure similar to that successfully applied for the synthesis of **3** and **4** was employed with **2** as the organic thienyl ligand [Scheme 2, Equation (2)]. Unfortunately, only a few green crystals of the yttrium thienylmethoxide $Y[OC(C_8H_5S_2)_3]_3(thf)_2$ (**5**) have been obtained in a very low yield (2%).This unsatisfying result may be explained by the more important steric hindrance of ligand system **2** bearing three bithienyl groups compared to that of **1** bearing three monothienyl groups and/or the difficulty to isolate the product. The ^{1}H NMR spectrum of **5** in benzene solution shows the characteristic signals of the protons of the bithienyl units and the methylene protons of the ligated tetrahydrofuran molecules (see Experimental Section).

Neodymium and Erbium Thienylmethoxides

With the aim of synthesizing a heteroleptic mixed amide-alkoxide compound, $Nd[N(SiMe_3)_2]_3$ was first treated with ligand **1** in a 1:1 ratio at ambient temperature in thf as solvent. However, we succeeded only in isolating the octahedrally coordinated neodymium thf-adduct, $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}\cdot thf$ (**6**), in the form of moisture-sensitive blue crystals, albeit in low yield (16%). Surprisingly, increasing the metal-to-ligand ratio to 1:3 did not improve the yield [Scheme 2, Equation (3)]. However, the yield could be significantly optimized to 73% upon treatment of the metal amide with alcohol **1** in a 1:6 ratio over two days. This finding clearly demonstrates the strong influence of the ligand concentration on the overall yield, which is important in shifting the equilibrium to the thienylmethoxide side.

The reaction of $Nd[N(SiMe_3)_2]_3$ with **2** in a 1:3 ratio [Scheme 2, Equation (4)] produced, after workup, green crystals of the octahedral compound $\{Nd[OC(C_8H_5S_2)_3]_3(thf)_3\}\cdot 4thf$ (**7**) in 50% yield. In this case, no attempt was made to increase the ligand ratio.

The variable-temperature ^{1}H NMR spectra of **6** and **7** recorded in $CDCl_3$ exhibit only broad peaks in the range 20 °C to 60 °C. This is probably due to the paramagnetic character of the neodymium metal centres. The ^{1}H NMR spectrum of compound **6**, at room temperature, shows a

broad signal at 7.5 ppm assigned to the protons of the thienyl ligands and three further broad resonances at 3.4, 2.7 and 0.8 ppm. These latter signals reveal the presence of methylene protons of tetrahydrofuran entities, either coordinated or not coordinated at the metal centre. The room-temperature ^{1}H NMR spectrum of **7** displays a multiplet for the protons of the bithienyl units centred at 7.1 ppm and four broad signals at 3.7, 1.8, 1.2 and 0.8 ppm corresponding to the different protons of the thf molecules, with or without bonding to neodymium.

A procedure similar to that applied for synthesis of $\{Nd[OC(C_4H_3S)_3]_3(thf)_3\}\cdot thf$ (**6**) and $\{Nd[OC(C_8H_5S_2)_3]_3(thf_3\}\cdot 4thf$ (**7**) was employed with erbium as metal [Scheme 2, Equations (3) and (4)]. The products, $Er[OC(C_4H_3S)_3]_3(thf)_3$ (**8**) or $Er[OC(C_8H_5S_2)_3]_3(thf)$ (**9**), were isolated in the form of moisture-sensitive pink (yield:14%) or brown (yield:15%) crystals, respectively.

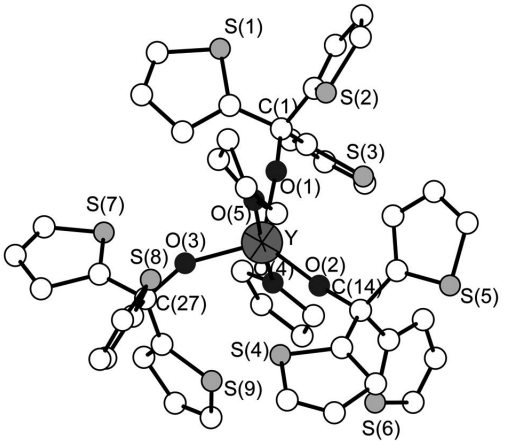
The variable-temperature ^{1}H NMR spectra of **8** and **9** in the range 20 °C to 60 °C in chloroform show, at room temperature, broad peaks due to the paramagnetic erbium metal centre. Nevertheless, for the compound **8** (and **9**), a multiplet at 7.0 ppm (7.0 ppm) can be assigned to the protons of the thienyl ligands and three broad peaks at 3.4, 1.2 and 0.9 ppm (3.7, 1.9, 1.2, 0.8 ppm) to the methylene protons of the thf molecules, with or without bonding to erbium.

X-ray Structure Determination of the Metal Thienylmethoxides

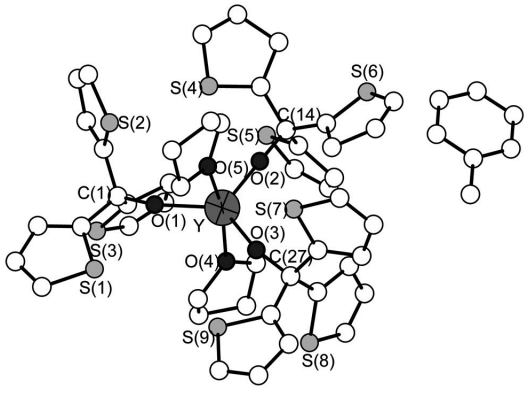
Yttrium Thienylmethoxides

Single-crystal X-ray structure determinations for compounds **3a** and **3b**, which crystallize at 5 °C from toluene as colourless crystals, were performed. The molecular structures exhibit exclusively mononuclear units with a five-coordinate yttrium atom in distorted trigonal-bipyramidal geometry: three carbinolato ligands in equatorial positions and two tetrahydrofuran molecules in axial positions are found (Figure 2). Due to packing effects, a toluene molecule can be included in the structure lattice, giving rise to another crystal structure, **3b**. Selected bond lengths and angles for **3a** and **3b** are assembled in Table 2. For $Y(OC(C_4H_3S)_3)_3(thf)_2$ (**3a**), the angles involving the pairs of $-O[C(C_4H_3S)_3]$ ligands are in the range 115.03(17)° to 123.48(16)°, and the O(thf)–Y–O[$C(C_4H_3S)_3$] angles vary from 87.28(15)° to 92.44(15)°. The Y–O[$C(C_4H_3S)_3$] bond lengths range from 2.091(4) Å to 2.111(3) Å, which is in good agreement with the distances found for related tris(2,6-dimethylphenoxido)yttrium complexes.[26,27] The Y–O(thf) bond lengths [2.386(4) Å and 2.404(4) Å] correspond to those observed in similar yttrium *tert*-butoxide complexes (2.41 Å).[18,27] The mean O–$C(C_4H_3S)_3$ distances of 1.381(3) Å are shorter than the value determined for carbinol **1** [1.440(4) Å]; this shortening is due to the additional charges on the oxygen atoms (δ^-) of the thienylmethoxides and the metal centre (δ^+). In contrast to many known yttrium alcoholates, which are dimeric[27] or are coordinated by three solvent molecules,[28] this alkoxide is mononuclear, and the metal centre is ligated by only two solvent molecules. No important alterations of the geometry of **3b** were observed relative to that of **3a** (see Table 2).

Light-brown single crystals of $Y[OC(C_4H_3S)_3]_3(py)_2$ (**4a**) and $\{Y[OC(C_4H_3S)_3]_3(py)_2\}\cdot$toluene (**4b**), in which the yttrium atom is fivefold coordinated, were obtained by concentration of a toluene (90%)/pyridine (10%) solvent mixture. As it can be seen in Figure 3, their trigonal-bipyramidal geometries are similar to those observed for compounds **3a** and **3b**, with an axial arrangement of the two pyridine ligands. Selected bond lengths and angles are available in Table 2. For $Y[OC(C_4H_3S)_3]_3(py)_2$ (**4a**), the $[(C_4H_3S)_3C]O$–Y–N angles are between 87.08(12)° and 93.99(11)°, and the sum of the $[(C_4H_3S)_3C]O$–Y–O[$C(C_3H_4S)_3$] angles is 359.74°. Despite the presence of pyridine instead of tetra-



3a

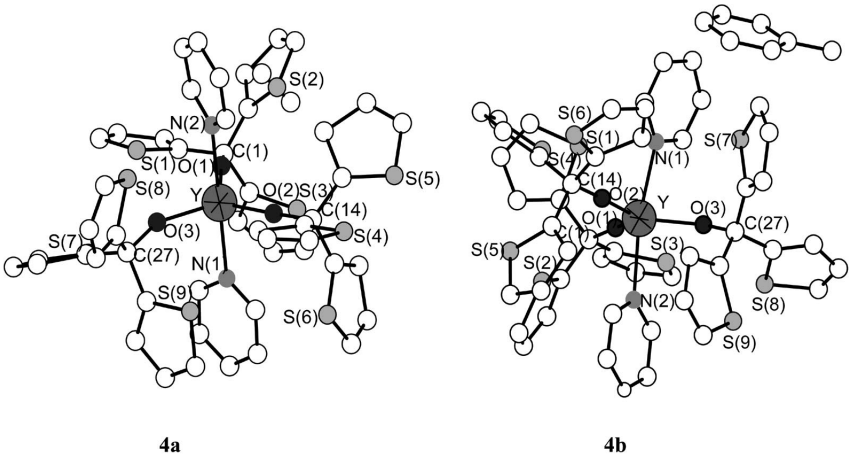


3b

Figure 2. Molecular structures of $Y[OC(C_4H_3S)_3]_3(thf)_2$ (**3a**) and $\{Y[OC(C_4H_3S)_3]_3(thf)_2\}\cdot$toluene (**3b**). Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for **3a**, **3b**, **4a**, **4b** and **5**.

	3a	**3b**		**4a**	**4b**	**5**	
Y–O(1)	2.091(4)	2.11104(18)	Y–O(1)	2.109(3)	2.092(2)	Y–O(1)	2.075(2)
Y–O(2)	2.083(4)	2.062(2)	Y–O(2)	2.100(3)	2.067(3)	Y–O(2)	2.106(3)
Y–O(3)	2.111(3)	2.082(2)	Y–O(3)	2.107(3)	2.098(3)	Y–O(3)	2.086(2)
Y–O(4)	2.386(4)	2.348(2)	Y–N(2)	2.520(3)	2.471(3)	Y–O(4)	2.348(2)
Y–O(5)	2.404(4)	2.349(2)	Y–N(1)	2.493(3)	2.481(3)	Y–O(5)	2.356(2)
O(1)–C(1)	1.339(7)	1.386(3)	O(1)–C(1)	1.399(5)	1.392(4)	O(1)–C(1)	1.390(4)
O(2)–C(14)	1.394(7)	1.382(3)	O(2)–C(14)	1.394(5)	1.413(4)	O(2)–C(27)	1.400(4)
O(3)–C(27)	1.409(7)	1.409(3)	O(3)–C(27)	1.406(5)	1.405(4)	O(3)–C(52)	1.397(4)
O(2)–Y–O(1)	121.24(17)	118.75(8)	O(2)–Y–O(1)	123.82(11)	122.26(10)	O(1)–Y–O(2)	120.25(9)
O(1)–Y–O(3)	115.03(17)	127.17(8)	O(3)–Y–O(1)	115.05(11)	122.06(10)	O(1)–Y–O(3)	110.10(10)
O(2)–Y–O(3)	123.48(16)	113.85(9)	O(2)–Y–O(3)	120.87(11)	115.56(10)	O(3)–Y–O(2)	128.64(9)
O(1)–Y–O(5)	87.28(15)	83.55(8)	N(2)–Y–O(1)	87.08(12)	91.94(11)	O(1)–Y–O(5)	91.93(9)
O(1)–Y–O(4)	90.43(17)	89.97(8)	O(1)–Y–N(1)	91.66(12)	85.06(11)	O(1)–Y–O(4)	89.98(9)
O(2)–Y–O(4)	92.44(15)	97.33(8)	O(2)–Y–N(1)	93.99(11)	95.31(10)	O(2)–Y–O(4)	87.46(9)
O(3)–Y–O(5)	90.05(16)	86.48(8)	O(3)–Y–N(2)	91.03(11)	86.56(11)	O(3)–Y–O(5)	90.65(9)
C(1)–O(1)–Y	166.8(4)	152.62(19)	C(1)–O(1)–Y	164.0(3)	161.6(3)	C(1)–O(1)–Y	173.9(2)
C(14)–O(2)–Y	174.3(4)	178.5(2)	C(14)–O(2)–Y	172.7(3)	172.4(2)	C(27)–O(2)–Y	161.4(2)
C(27)–O(3)–Y	153.6(4)	159.16(18)	C(27)–O(3)–Y	154.5(2)	149.1(2)	C(52)–O(3)–Y	168.4(2)
O(4)–Y–O(5)	177.72(15)	166.50(7)	N(1)–Y–N(2)	178.72(12)	169.34(11)	O(4)–Y–O(5)	174.28(9)



4a **4b**

Figure 3. Molecular structures of $Y[OC(C_4H_3S)_3]_3(py)_2$ (**4a**) and $\{Y[OC(C_4H_3S)_3]_3(py)_2\}$·toluene (**4b**).

hydrofuran, no significant variations of the $[(C_4H_3S)_3C]O$–Y–$O[C(C_4H_3S)_3]$ and $[(C_4H_3S)_3]C$)–O–Y angles or Y–$O[C(C_4H_3S)_3]$ bond lengths are observed. The Y–N distances lie in the range 2.493(3)–2.520(3) Å. Again, the mean O–$C(C_4H_3S)_3$ lengths of 1.400(1) Å are shorter than the value obtained for the starting compound **1**. In the second solid-state structure, **4b**, one molecule of toluene is included: only some minor variations of the angles are observed (Table 2).

Green single crystals of $Y[OC(C_8H_5S_2)_3]_3(thf)_2$ (**5**) were obtained by concentration of the solvent. Despite the fact that the ligand $–OC(C_8H_5S_2)_3$ is sterically more demanding than $–OC(C_4H_3S)_3$, the molecular structure exhibits again distorted trigonal-bipyramidal geometry around the yttrium atom with three equatorial carbinolato ligands and two axial molecules of tetrahydrofuran (Figure 4). Selected bond lengths and angles are available in Table 2. The sum of the $[(C_8H_5S_2)_3C]O$–Y–$O[C(C_8H_5S_2)_3]$ angles is 359.00(9)° and the O(thf)–Y–$O[C(C_8H_5S_2)_3]$ angles are be-

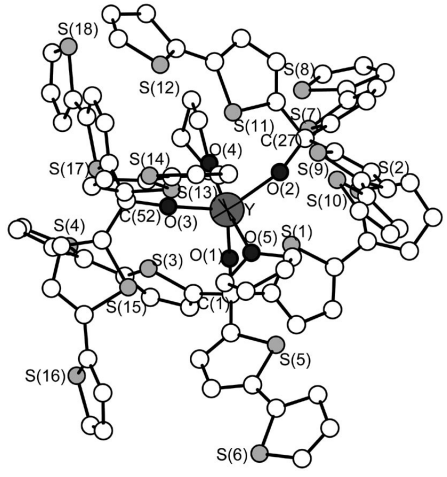


Figure 4. Molecular structure of $Y[OC(C_8H_5S_2)_3]_3(thf)_2$ (**5**). Hydrogen atoms are omitted for clarity.

tween 87.46(9)° and 91.93(9)°. The Y–O[C($C_8H_5S_2$)$_3$] and Y–O(thf) bond lengths are in the range 2.075(2)–2.106(3) Å and 2.348(2)–2.356(2) Å, respectively. They are in similar ranges with these observed for **3a**, **4a** and **4b**. The O–C(C_8H_5S)$_2$ distances, which average 1.396(0) Å, are shorter than those for carbinol **2**, which have a mean value of 1.440(8) Å.

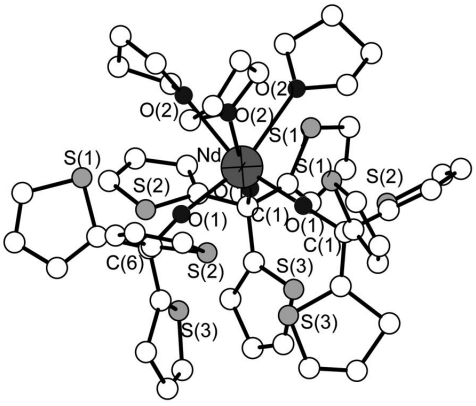
Neodymium Thienylmethoxides

Blue single crystals of **6** were grown from a tetrahydrofuran solution at 5 °C. Selected bond lengths and angles are gathered in Table 3. The structure determination reveals a monomer with an approximately octahedral geometry around the neodymium atom: this metal centre is surrounded by three tris(2-thienyl)methoxido ligands and three tetrahydrofuran molecules in a facial arrangement. The molecule is situated on a threefold axis in the crystal. An additional molecule of tetrahydrofuran is situated in the crystal structure with no interaction with the molecule (Figure 5). Evidently, neodymium(3+) is wrapped up by the ligand, which leads to a quite low coordination number. Moreover, the bulky ligands and their high electronic densities prevent the formation of a coordination polymer. The overall structure of **6** is similar to that of Sm(O–2,6-*i*Pr$_2$C$_6$H$_3$)$_3$(thf)$_3$[29] and Sm(O2,4,6Me$_3$C$_6$H$_2$)$_3$(thf)$_3$.[30] The [(C_4H_3S)$_3$C]O–Nd–O[C(C_4H_3S)$_3$] and O(thf)–Nd–O(thf) bond angles [100.81(6)°, 73.55(6)°, respectively] are smaller than those for Sm(O–2,4,6–Me$_3$C$_6$H$_2$)$_3$(thf)$_3$ [103.39(13)° and 77.46(11)°]. The Nd–O[C(C_4H_3S)$_3$] distances [2.1861(13) Å] are in the range of those obtained for six-coordinate Nd(OC*t*Bu$_2$CH$_2$PMe$_2$)$_3$ [2.174(2) Å],[31] or with five-coordinate Nd(tritox)$_3$(CH_3CN)$_2$[32] [2.149(5)–2.171(5) Å]. However, they are shorter than those in Nd$_2$(O–2,6-*i*Pr$_2$C$_6$H$_3$)$_6$ [2.211(8) Å],[23] a dinuclear compound possessing bridging alcoholato ligands. The Nd–O(thf) bond lengths [2.6202(15) Å] are shorter than those obtained for [Nd$_3$(μ_3-O*t*Bu)$_2$(μ_2-O*t*Bu)$_3$(O*t*Bu)$_4$(thf)$_2$] [2.661(4) Å].[33] The O–C(C_4H_3S)$_3$ distances [1.389(2) Å] are also shorter than those obtained for the star-shaped compound **1**: this shortening is due to the additional charges on the oxygen atoms (δ^-) of the thienylmethoxides and the metal centre (δ^+). The [(C_4H_3S)$_3$C]O–Nd–O(thf) bond angles are 92.82(6)°. The C(1)–O[C(C_4H_3S)$_3$]–Nd angles [169.90(13)°] are in the range of these observed for the C–O–Y angles of compounds **3a**, **3b**, **4a**, **4b** and **5**.

Table 3. Selected bond lengths [Å] and angles [°] for **6** and **7**.

6		**7**	
Nd–O(1)	2.1861(13)	Nd–O(1)	2.173(5)
Nd–O(2)	2.6202(15)	Nd–O(2)	2.203(5)
		Nd–O(3)	2.202(5)
		Nd–O(4)	2.563(5)
		Nd–O(5)	2.558(5)
		Nd–O(6)	2.550(5)
O(1)–C(1)	1.389(2)	O(1)–C(1)	1.380(9)
		O(2)–C(26)	1.401(9)
		O(3)–C(51)	1.393(9)
O(1)–Nd–O(1)	100.81(6)	O(1)–Nd–O(3)	98.31(18)
O(1)–Nd–O(2)	92.82(6)	O(1)–Nd–O(2)	102.00(19)
O(2)–Nd–O(2)	73.55(6)	O(3)–Nd–O(6)	87.61(17)
C(1)–O(1)–Nd	169.90(13)	O(2)–Nd–O(5)	89.10(17)
		O(5)–Nd–O(4)	85.38(17)
		O(6)–Nd–O(4)	71.61(18)
		C(1)–O(1)–Nd	176.1(5)
		C(26)–O(2)–Nd	174.9(4)
		C(51)–O(3)–Nd	161.1(4)

Green single crystals of [Nd(OC($C_8H_5S_2$)$_3$)$_3$(thf)$_3$]·4thf (**7**) were grown from a concentrated tetrahydrofuran solution at –5 °C. The facial coordination geometry around the metal is similar to that in [Nd(OC(C_4H_3S)$_3$)$_3$(thf)$_3$]·thf (**6**) (Figure 5). Selected bond lengths and angles are listed in Table 3. Four additional molecules of tetrahydrofuran are in the lattice with no interaction with the central molecule



6

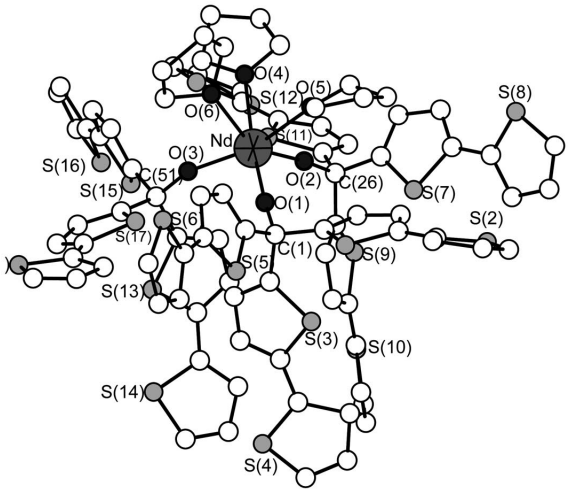


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Figure 5. Molecular structures of {Nd[OC(C_4H_3S)$_3$]$_3$(thf)$_3$}·thf (**6**) and {Nd[OC($C_8H_5S_2$)$_3$]$_3$(thf)$_3$}·4thf (**7**). Hydrogen atoms are omitted for clarity.

(Figure 5). Evidently, neodymium(3+) is also wrapped up by the ligand, leading to a quite low coordination number. The Nd–O[C($C_8H_5S_2$)$_3$] bond lengths [2.173(5) to 2.203(5) Å] correspond to those observed for **6**; nevertheless, the Nd–O(thf) lengths are shorter [2.550(5) to 2.563(5) Å]. The O–C($C_8H_5S_2$)$_3$ distances, which average 1.392(2) Å, are also shorter than the value obtained for alcohol **2**. In comparison to compound **6**, the angles O(thf)–Nd–O[C($C_8H_5S_2$)$_3$] [87.61(7)°–89.10(17)°] are more acute, the O(thf)–Nd–O(thf) angles are in the range 71.61(18)°–85.38(17)°, and the [($C_8H_5S_2$)$_3$C]O–Nd–O[C($C_8H_5S_2$)$_3$] angles vary from 98.31(18)° to 102.00(19)°. The ($C_8H_5S_2$)$_3$C–O–Nd angles are between 161.1(4)° and 176.1(5)°. These differences of angles from those in {Nd[OC(C_4H_3S)$_3$]$_3$(thf)$_3$}·thf (**6**) could be explained by the enhanced steric hindrance of the ligands in **7**.

Erbium Thienylmethoxides

Unfortunately, the X-ray structure determinations for Er[OC(C_4H_3S)$_3$]$_3$(thf)$_3$ (**8**) and Er[OC($C_8H_5S_2$)$_3$]$_3$(thf) (**9**) could not be refined in a satisfying manner because of the poor quality of the crystals. Nevertheless, the data allow us to conclude unambiguously that the coordination sphere around the erbium atom of **8** is octahedral: it includes three tris(2-thienyl)methoxido ligands and three tetrahydrofuran molecules. A tetrahedral oxygen geometry was established for **9**, consisting of three tris(2,2′-bithienyl-5-yl)-methoxido ligands and one tetrahydrofuran molecule coordinated around the Er^{III} centre.

Note that the coordination number of mononuclear erbium alkoxides is very variable and may range from 4 to 8.[34–36] The octahedral geometry determined for **8** is in good agreement with that found for Nd[OC(C_4H_3S)$_3$]$_3$-(thf)$_3$ (**6**) (see above). The overall structure of low-coordinate **9** is best compared with that of the tetrahedral compound tris(2,6-di-*tert*-butyl-4-methylphenolato-*O*)(thf)-erbium·toluene,[34] and it also similar to that of the tetrahedral compound Sm(O–2,6-*tert*-$Bu_2C_6H_3$)$_3$(thf).[37]

Conclusions and Perspectives

The carbinols tris(2-thienyl)methanol (**1**) and tris(2,2′-bithienyl-5-yl)methanol (**2**) produce, upon treatment with the appropriate rare earth amides, exclusively mononuclear thienylmethoxides of yttrium, neodymium and erbium. We have shown that the geometry around the yttrium centre is trigonal-bipyramidal for **3a**, **3b**, **4a**, **4b** and **5**. The neodymium thienylmethoxides **6** and **7**, in which the coordination sphere around the metal is octahedral, exhibit a facial ligand arrangement. Even though no well-refined X-ray structures of **8** and **9** could be obtained, the first calculations allow us to conclude that **8** possesses the same geometry as **6** and indicate that a tetrahedral geometry is observed for erbium carbinolate **9**.

Detailed studies of the luminescence and electrochemical properties of these metal thienylmethoxides are in progress. These physicochemical investigations are currently followed by the syntheses of and crystal structure determinations for other rare earth metal (Sm^{3+}, Eu^{3+}) thienylmethoxides.

Experimental Section

General: All reactions were performed under nitrogen in a Schlenk apparatus. The solvents (thf, toluene, diethyl ether, benzene) were distilled from sodium and kept under nitrogen. Pyridine was distilled from KOH and kept under nitrogen. Y[N($SiMe_3$)$_2$]$_3$, Nd[N($SiMe_3$)$_2$]$_3$,[25] tris(2-thienyl)methanol[17] and tris(2,2′-bithienyl-5-yl)methanol[12] were prepared according to literature procedures. The ^{1}H NMR spectra were recorded with a Bruker ACF-NMR (200 MHz) or a Bruker Avance 400 spectrometer (400 MHz, H,H-COSY). The UV/Vis spectra were obtained with a Perkin–Elmer Lambda 35 spectrometer. Analytical data were measured with a LECO CHN–900 instrument. Some samples repeatedly showed a considerably different content of carbon, hydrogen and nitrogen than calculated; these results have not been listed. The irreproducibility of analytical data may be due to the high sensitivity of the compounds to air. Mass spectra (EI, 150 V) of compounds **6**, **8** and **9** were obtained with a Finnigan MAT 95 S spectrometer. Only characteristic fragments containing the isotopes of highest abundance are listed.

Crystallographic Details: The data collection was performed with an X8 ApexII CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å). Structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with SHELX-97.[38] Drawings were made with Diamond.[39] All crystals of the compounds started growing at 5°C during a period of one week. No sign of deterioration during storage under nitrogen was observed. Crystallographic data for the structure determinations are listed in Table 4 and Table 5, and relevant bond lengths and angles are given in Tables 1, 2 and 3.

CCDC-665115, -665116, -665117, -665118, -665119, -665120, -665121, -665122, -665123 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Y[OC(C_4H_3S)$_3$]$_3$(thf)$_2$ (3a): To a solution of three equivalents of tris(2-thienyl)methanol (1.46 g, 5.2 mmol) in thf (20 mL) was added one equivalent of Y[N($SiMe_3$)$_2$]$_3$ (1 g, 1.7 mmol) in thf (30 mL). The mixture was stirred at room temperature for two days. The solvent was evaporated, and a brown solid was obtained. The product was subsequently recrystallized as colourless crystals from toluene at 5°C. The isolated yield is 23% (420 mg). ^{1}H NMR (400.13 MHz, C_6D_6): δ = 7.1 (br. s, 9 H, 5-H), 6.9 (br. s, 9 H, 3-H), 6.7 (br. s, 9 H, 4-H), 3.7 (thf), 1.4 (thf) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-4} M): λ (ε, L mol^{-1} cm^{-1}) = 257 (309.507 × 10^2) nm. $C_{47}H_{43}O_5S_9Y$ (1065.26): calcd. C 52.99, H 4.07; found C 49.43, H 3.28.

{Y[OC(C_4H_3S)$_3$]$_3$(thf)$_2$}·Toluene (3b): The isolated yield is 37% (722 mg, colourless crystals). ^{1}H NMR (400.13 MHz, C_6D_6): δ = 7.1 (dd, $^3J_{H5,H4}$ = 6 Hz and $^4J_{H5,H3}$ = 1.2 Hz, 9 H, 5-H), 6.9 (dd, $^3J_{H3,H4}$ = 5.2 Hz and $^4J_{H3,H5}$ = 0.8 Hz, 9 H, 3-H), 6.7 (dd, $^3J_{H4,H5}$ = 8 Hz and $^3J_{H4,H3}$ = 4 Hz, 9 H, 4-H), 7.0 (toluene), 3.7 (thf), 2.1 (toluene), 1.1 (thf) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-4} M): λ (ε, L mol^{-1} cm^{-1}) = 251 (291.095 × 10^2) nm. $C_{54}H_{51}O_5S_9Y$ (1157.40): calcd. C 56.03, H 4.44; found C 54.34, H 4.08.

Y[OC(C_4H_3S)$_3$]$_3$(py)$_2$ (4a): To a solution of three equivalents of tris(2-thienyl)methanol (1.46 g, 5.2 mmol) in toluene (25 mL) was added one equivalent of Y[N($SiMe_3$)$_2$]$_3$ (1 g, 1.7 mmol) in toluene

Table 4. X-ray crystallographic and refinement data for **1**, **2**, **3a** and **3b**.

Compounds	**1**	**2**	**3a**	**3b**
Empirical formula	$C_{13}H_{10}OS_3$	$C_{25}H_{16}OS_6$	$C_{47}H_{43}O_5S_9Y$	$C_{54}H_{51}O_5S_9Y$
Formula weight	278.39	524.74	1065.26	1157.40
Temperature [K]	293(2)	103(2)	293(2)	103(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1$
a [Å]	11.147(2)	16.217(2)	20.889(4)	12.7243(8)
b [Å]	7.4240(10)	6.0586(7)	14.421(3)	15.9300(9)
c [Å]	15.623(3)	23.280(3)	16.190(3)	14.3268(9)
α [°]	90	90	90	90
β [°]	100.24(3)	98.824(5)	94.75(3)	114.404(2)
γ [°]	90	90	90	90
Volume [Å^3]	1272.3(4)	2260.2(5)	4860.4(17)	2644.6(3)
Z	4	4	4	2
$\rho_{calcd.}$ [g cm^{-3}]	1.453	1.542	1.456	1.453
μ [mm^{-1}]	0.561	0.623	1.631	1.505
$F(000)$	576	1080	2192	1196
Crystal size [mm]	0.7 × 0.6 × 0.3	0.25 × 0.5 × 0.65	0.25 × 0.4 × 0.55	0.3 × 0.5 × 0.65
θ range for data collection [°]	1.86 to 23.93	1.27 to 23.25	1.89 to 24.11	1.56 to 36.80
Reflections collected	7714	26879	28041	63311
Independent reflections	1967	3243	7593	23073
R(int)	0.2185	0.1379	0.0738	0.0342
Completeness to θ = 23.25° [%]	99.2	99.7	98.2	99.0
Absorption correction	none	none	semi-empirical from equivalents	semi-empirical from equivalents
Data/restraints/parameters	1967/0/158	3243/8/305	7593/0/559	23073/9/629
Goodness-of-fit on F^2	1.064	1.055	1.972	1.440
Final R indices	R_1 = 0.0567,	R_1 = 0.0594,	R_1 = 0.0742,	R_1 = 0.0535,
[$I > 2\sigma(I)$]	wR_2 = 0.1498	wR_2 = 0.1297	wR_2 = 0.2067	wR_2 = 0.1460
Largest diff. peak and hole [e Å^{-3}]	0.717 and –0.376	0.408 and –0.537	1.981 and –1.057	3.226 and –1.747
Absolute structure parameter				–0.002(3)

Table 5. X-ray crystallographic and refinement data for **4a**, **4b**, **5**, **6**, **7**.

Compounds	**4a**	**4b**	**5**	**6**	**7**
Empirical formula	$C_{49}H_{37}N_2O_3S_9Y$	$C_{56}H_{45}N_2O_3S_9Y$	$C_{83}H_{62}O_5S_{18}Y$	$C_{55}H_{59}NdO_7S_9$	$C_{103}H_{101}NdO_{10}S_{18}$
Formula weight	1079.26	1171.39	1805.32	1264.80	2220.16
Temperature [K]	293(2)	103(2)	103(2)	143(2)	103(2)
Crystal system	monoclinic	monoclinic	monoclinic	rhombohedral	triclinic
Space group	$P2_1/c$	$P2_1$	$P2_1/n$	$R3$	$P\bar{1}$
a [Å]	20.802(4)	12.4487(8)	12.5246(16)	13.9688(6)	13.9062(3)
b [Å]	14.573(3)	16.2321(10)	15.182(2)	13.9688(6)	17.7968(4)
c [Å]	16.041(3)	14.1860(7)	41.606(5)	24.6314(10)	20.7081(4)
α [°]	90	90	90	90	90.9370(10)
β [°]	93.55(3)	112.311(2)	97.480(2)	90	102.8770(10)
γ [°]	90	90	90	120	93.1290(10)
Volume [Å^3]	4853.6(17)	2651.9(3)	7843.9(18)	4162.3(3)	4986.48(18)
Z	4	2	4	3	2
$\rho_{calcd.}$ [g cm^{-3}]	1.477	1.467	1.529	1.514	1.479
μ [mm^{-1}]	1.633	1.501	1.276	1.325	0.957
$F(000)$	2208	1204	3708	1947	2294
Crystal size [mm]	0.35 × 0.45 × 0.6	0.2 × 0.4 × 0.55	0.3 × 0.5 × 0.65	0.3 × 0.5 × 0.55	0.3 × 0.6 × 0.7
θ range for data collection [°]	1.89 to 24.13	1.77 to 29.05	0.99 to 29.79	1.88 to 45.44	1.01 to 19.61
Reflections collected	30211	24074	104589	102475	46816
Independent reflections	7590	11138	22216	14318	8779
R(int)	0.0517	0.0427	0.0785	0.0292	0.0331
Completeness to θ = 23.25° [%]	98.0	85.9	98.9	100.0	99.9
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
Data/restraints/parameters	7590/48/620	11138/9/647	22216/32/994	14318/1/212	8779/50/1164
Goodness-of-fit on F^2	1.055	0.999	0.992	1.491	1.038
Final R indices	R_1 = 0.0497,	R_1 = 0.0429,	R_1 = 0.0533,	R_1 = 0.0446,	R_1 = 0.0477,
[$I > 2\sigma(I)$]	wR_2 = 0.1291	wR_2 = 0.0971	wR_2 = 0.1207	wR_2 = 0.1203	wR_2 = 0.1201
Largest diff. peak and hole [e Å^{-3}]	1.813 and –1.397	1.130 and –0.897	1.392 and –1.073	5.174 and –3.235	1.574 and –0.804
Absolute structure parameter		0.001(4)		0.009(8)	

(25 mL) and pyridine (5 mL). The mixture was stirred at room temperature for two days. A brown solution was obtained. The solution was concentrated, and light-brown crystals were obtained at 5 °C a few days later. The isolated yield is 10% (180 mg). ^{1}H NMR (400.13 MHz, C_6D_6): δ = 6.9 (dd, $^3J_{H5,H4}$ = 3.5 Hz and $^4J_{H5,H3}$ = 0.8 Hz, 9 H, 5-H), 6.8 (dd, $^3J_{H3,H4}$ = 4.7 Hz and $^4J_{H3,H5}$ = 0.8 Hz, 9 H, 3-H), 6.6 (dd, $^3J_{H4,H3}$ = 4.7 Hz and $^3J_{H4,H5}$ = 3.5 Hz, 9 H, 4-H), 8.4 (py), 6.9 (py), 6.6 (py) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-4} M): λ (ε, L mol^{-1} cm^{-1}) = 250 (289.666×10^2) nm. $C_{49}H_{37}N_2O_3S_9Y$ (1079.26): calcd. C 54.53, H 3.46, N 2.60; the analysis could not be performed because of the air-sensitivity of the crystals.

{Y[OC(C$_4$H$_3$S)$_3$]$_3$(py)$_2$}·Toluene (4b): The isolated yield is 61% (1.220 g, light-brown crystals). ^{1}H NMR (400.13 MHz, C_6D_6): δ = 6.9 (d, $^3J_{H5,H3}$ = 3.2 Hz, 9 H, 5-H), 6.8 (d, $^3J_{H3,H4}$ = 4.8 Hz, 9 H, 3-H), 6.6 (dd, $^3J_{H4,H3}$ = 4.8 and $^3J_{H5,H3}$ = 3.2 Hz, 9 H, 4-H), 8.4 (py), 6.9 (py), 6.6 (py), 7.0 (toluene), 2.1 (toluene) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-4} M): λ (ε, L mol^{-1} cm^{-1}) = 252 (248.414×10^2) nm. $C_{56}H_{45}N_2O_3S_9Y$ (1171.39): calcd. C 57.29, H 3.87, N 2.39; found C 57.06, H 3.51, N 3.52.

Y[OC(C$_8$H$_5$S$_2$)$_3$]$_3$(thf)$_2$ (5): To a solution of three equivalents of tris(2,2′-bithienyl-5-yl)methanol (0.300 g, 0.57 mmol) in thf (20 mL) was added one equivalent of Y[N(SiMe$_3$)$_2$]$_3$ (0.108 g, 0.19 mmol) in thf (10 mL). The mixture was stirred at room temperature for two days. The solvent was evaporated; a green solid was obtained. The product was subsequently recrystallized from toluene as green crystals. The isolated yield is 2% (6 mg). ^{1}H NMR (200.13 MHz, C_6D_6): δ = 6.9 (dd, $^3J_{H5',H4'}$ = 4.5 Hz and $^4J_{H5',H3'}$ = 0.8 Hz, 9 H, 5′-H), 6.8 (d, $^3J_{H3,H4}$ = 3.7 Hz, 9 H, 3-H), 6.8 (d, $^3J_{H4,H3}$ = 3.7 Hz, 9 H, 4-H), 6.7 (dd, $^3J_{H3',H4'}$ = 3.7 Hz and $^4J_{H3',H5'}$ = 0.8 Hz, 9 H, 3′-H), 6.6 (dd, $^3J_{H4',H5'}$ = 5.0 Hz and $^3J_{H4',H3'}$ = 3.7 Hz, 9 H, 4′-H), 3.6 (thf), 1.4 (thf) ppm. $C_{83}H_{62}O_5S_{18}Y$ (1805.32): calcd. C 55.22, H 3.43; found C 55.48, H 3.10.

{Nd[OC(C$_4$H$_3$S)$_3$]$_3$(thf)$_3$}·thf (6)

Method 1: To a solution of tris(2-thienyl)methanol (0.244 g, 0.87 mmol) in thf (10 mL) was added Nd[N(SiMe$_3$)$_2$]$_3$ (0.547 g, 0.87 mmol) in thf (15 mL). The mixture was stirred at room temperature for two days. The solution was concentrated, and blue crystals were obtained at 5 °C a few days later. The isolated yield is 16% (172 mg).

Method 2: To a solution of three equivalents of tris(2-thienyl)methanol (0.498 g, 1.79 mmol) in thf (20 mL) was added one equivalent of Nd[N(SiMe$_3$)$_2$]$_3$ (0.372 g, 0.59 mmol) in thf (20 mL). The mixture was stirred at room temperature for two days. The solution was concentrated, and blue crystals were obtained at 5 °C a few days later. The isolated yield is 12% (91 mg).

Method 3: To a solution of six equivalents of tris(2-thienyl)methanol (0.534 g, 1.92 mmol) in thf (20 mL) was added one equivalent of Nd[N(SiMe$_3$)$_2$]$_3$ (0.200 g, 0.32 mmol) in thf (20 mL). The mixture was stirred at room temperature for two days. Blue crystals were obtained at 5 °C several days later. The isolated yield is 72% (292 mg).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.5 (br. s, 27 H, protons of thienyl units), 3.4 (br. s, 7 H, thf), 2.7 (br. s, 17 H, thf), 0.8 (br. s, 9 H, thf) ppm. MS (EI, ^{144}Nd): *m*/*z* (%) = 960 (16) [M – CH_3 – (thf)$_3$ – thf]$^+$, 1180 (0.5) [M – thf]$^{\cdot+}$. UV/Vis (190–1100 nm, CH_2Cl_2, 9.41×10^{-5} M): λ (ε, L mol^{-1} cm^{-1}) = 237 (2909.55×10^3) nm. $C_{55}H_{59}NdO_9S_9$ (1264.80): calcd. C 52.22, H 4.66, Nd 11.40; found C 48.63, H 3.40, Nd 11.26.

{Nd[OC(C$_8$H$_5$S$_2$)$_3$]$_3$(thf)$_3$}·4thf (7): To a solution of three equivalents of tris(2,2′-bithienyl-5-yl)methanol (0.400 g, 0.70 mmol) in thf (15 mL) was added one equivalent of Nd[N(SiMe$_3$)$_2$]$_3$ (0.158 g, 0.25 mmol) in thf (10 mL). The mixture was stirred at room temperature for two days. The solution was concentrated. Green crystals were obtained at 5 °C a few days later. The isolated yield is 50% (278 mg). ^{1}H NMR (400.13 MHz, $CDCl_3$): 7.1 (m, 45 H, protons of bithienyl units), 3.7 (br. s, 14 H, thf), 1.8 (br. s, 14 H, thf), 1.2 (br. s, 21 H, thf), 0.8 (br. s, 7 H, thf) ppm. UV/Vis (190–1100 nm, CH_2Cl_2, 8.70×10^{-5} M): λ (ε, L mol^{-1} cm^{-1}) = 232, 312 (2397.95×10^3, 1021.87×10^3) nm. $C_{103}H_{101}NdO_{10}S_{18}$ (2220.16): calcd. C 55.71, H 4.54, Nd 6.49; the analysis could not be performed because of the air-sensitivity of the crystals.

Er[OC(C$_4$H$_3$S)$_3$]$_3$(thf)$_3$ (8): To a solution of three equivalents of tris(2-thienyl)methanol (1.185 g, 4.26 mmol) in thf (20 mL) was added one equivalent of Er[N(SiMe$_3$)$_2$]$_3$ (0.920 g, 1.47 mmol) in thf (50 mL). The mixture was stirred at room temperature for two days. The solution was concentrated, and pink crystals were obtained at 5 °C a few days later. The isolated yield is 14% (243 mg). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.0 (m, 27 H, protons of thienyl units), 3.5 (br. s, 3 H, thf), 1.2 (br. s, 14 H, thf), 0.9 (br. s, 7 H, thf) ppm. MS (EI, ^{166}Er): *m*/*z* (%) = 166 (1.5) [M – (OC(C$_4$H$_3$S)$_3$)$_3$ – (thf)$_3$]$^+$, 277 (5) [M – Er – (OC(C$_4$H$_3$S)$_3$)$_2$ – (thf)$_3$]$^+$. UV/Vis (190–1100 nm, CH_2Cl_2, 10^{-6} M): λ (ε, L mol^{-1} cm^{-1}) = 243 (2254.65×10^3) nm. $C_{47}H_{43}O_5S_9Er$ (1214.26): C 50.40, H 4.20; the analysis could not be performed because of the air-sensitivity of the crystals.

Er[OC(C$_8$H$_5$S$_2$)$_3$]$_3$(thf) (9): To a solution of three equivalents of tris(2,2′-bithienyl-5-yl)methanol (0.590 g, 1.1 mmol) in thf (20 mL) was added one equivalent of Er[N(SiMe$_3$)$_2$]$_3$ (0.242 g, 0.37 mmol) in thf (20 mL). The mixture was stirred at room temperature for two days. The solution was concentrated. Brown crystals were obtained at 5 °C a few days later. The isolated yield is 15% (100 mg). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.1 (m, 45 H, protons of bithienyl units), 3.7 (br. s, 5 H, thf), 1.9 (br. s, 5 H, thf), 1.2 (br. s, 10 H, thf), 0.8 (br. s, 4 H, thf) ppm. MS (EI, ^{166}Er): *m*/*z* (%) = 523 (10) [M – Er – [OC(C$_8$H$_5$S$_2$)$_3$]$_2$ – thf]$^+$, 166 (17) [M – [OC(C$_8$H$_5$S$_2$)$_3$]$_3$ – thf]$^+$. UV/Vis (190–1100 nm, CH_2Cl_2, 1.07×10^{-6} M): λ (ε, L mol^{-1} cm^{-1}) = 233, 262 (1515.51×10^3, 708.12×10^3) nm. $C_{79}H_{53}O_4S_{18}Er$ (1810.73): C 52.40, H 2.95; found: C 49.99, H 3.38.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR spectra for **3a**, **3b**, **4a**, **4b**, **5**, **6**, **7**, **8** and **9**; molecular structures of **1**, **2**, **3a**, **3b**, **4a**, **4b**, **5**, **6** and **7**.

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