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Metallosupramolecular Complexes Derived from Bis(benzene-*o*-dithiol) Ligands

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Abstract: Contrary to its catechol analogue, the 1,5-naphthalenediamido-bridged bis(benzene-*o*-dithiol) ligand H_4-**3** does not yield $[Ti_4L_6]^{8-}$ clusters when reacted with Ti^{4+} starting materials, but instead gives dinuclear, triple-stranded complexes of type $[Ti_2L_3]^{4-}$. The molecular structures of such complexes differ depending on the size of the counterions employed. The formation of both *meso* complexes (Λ,Δ or Δ,Λ isomers) and of dinuclear triple-stranded helicates (Λ,Λ or Δ,Δ isomers) was observed. Molecular-modeling calculations show energetically close minima for the *meso* complex and the corresponding helicate. In spite of the structural differences in the solid state, proton NMR spectra reveal C_3 symmetry for all three complex anions. Metal–donor interactions mainly dictate the coordination behavior, whereas the topology of the ligand has less influence. In addition, the dinuclear complex $[Ti_2(\mathbf{8})_3]^{4-}$ with the unsymmetrical bis(benzene-*o*-dithiol) ligand H_4-**8** has been prepared. The unsymmetrical ligand can lead to four different stereoisomers when forming dinuclear triple-stranded complexes of type $[Ti_2(\mathbf{8})_3]^{4-}$, two of which have been observed in solution.

Keywords: benzene-*o*-dithiol · coordination compounds · molecular modeling · self-assembly · supramolecular chemistry

Introduction

The spontaneous self-assembly of coordination compounds forming metallosupramolecular architectures has attracted considerable interest. A number of spectacular molecules have emerged from research in this area over the last decade.[1] Several supramolecular structural motifs, such as helicates,[2] boxes,[3] squares,[4] molecular containers,[5] and others,[6] have been prepared using metal-controlled self-assembly reactions. Among these, metallohelicates have received special interest due to the presence of the helix motif in nature.

In 1987, Lehn et al. reported the first structurally characterized metallohelicate containing two tris(bipyridine) ligands and three Cu^I ions.[7] Since then, metallosupramolecular dinuclear double- and triple-stranded helical complexes containing amine or catecholato[2,8] donor groups have been studied in detail. Related ligands and complexes derived from benzene-*o*-dithiol donor groups[1e] remained rare in supramolecular chemistry most likely due to the difficulties encountered during the preparation of the bis- or tris(benzene-*o*-dithiol) ligands.

In 1995 we reported a method for the *ortho* functionalization of benzene-*o*-dithiol that allowed the preparation of the first bis- and tris(benzene-*o*-dithiol) ligands.[9] By using these ligands we prepared dinuclear triple-stranded helicates with bis(benzene-*o*-dithiolato)[10] and mixed benzene-*o*-dithiolato/catecholato ligands.[11]

The tris(benzene-*o*-dithiolato) complexes are of special interest due to the possible variation in the coordination geometry from octahedral to trigonal-prismatic depending on the formal oxidation state of the metal center. This type of geometry change has been discussed in detail for tris(ben-

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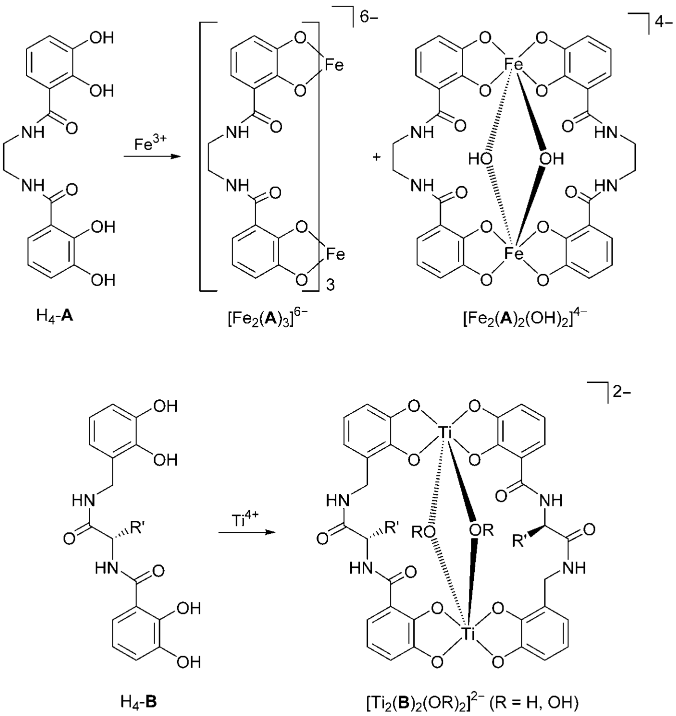
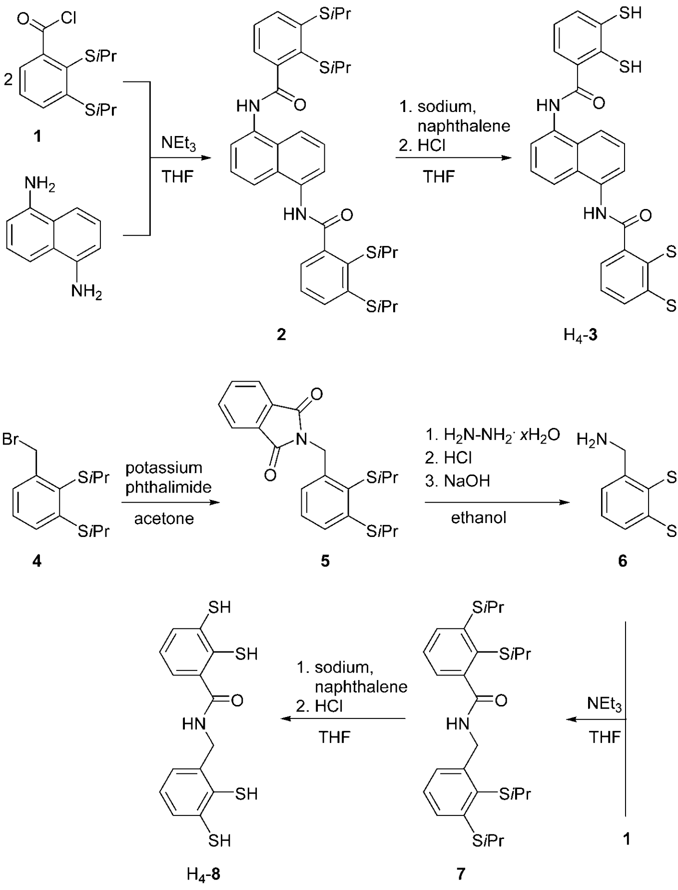
zene-*o*-dithiolato) complexes of type $[M(bdt)_3]^{n-}$ (M = Mo,[12] W;[13] bdt = benzene-*o*-dithiolato dianion).

Up to now only a few ligands have been known to generate different structural motifs when used in metal-controlled self-assembly reactions. Enemark and Stack described the dicatechol ligand H_4-**A** (Scheme 1), which is capable of forming a triple-stranded helicate $[Fe_2(\mathbf{A})_3]^{6-}$ or a dinuclear double-stranded complex $[Fe_2(\mathbf{A})_2(OH)_2]^{4-}$ depending on the metal/ligand ratio used.[14] The analogous bis(benzene-*o*-dithiol) ligand reacts with Ti^{4+} to yield exclusively the triple-stranded helicate regardless of the metal/ligand ratio used.[10a] Albrecht et al. prepared a series of amino acid bridged dicatechol ligands of type H_4-**B** (Scheme 1) that exclusively form dinuclear double-stranded complexes $[Ti_2(\mathbf{B})_2(OR)_2]^{2-}$ (R = H, CH_3) with two bridging alkoxy coligands OR^-. Depending on the orientation of the directional ligands, a mixture of geometrical and stereoisomers was obtained but no triple-stranded complexes were observed with ligands of type $\mathbf{B}^{4-}$.[15]



Scheme 1. Dicatechol ligands H_4-**A** and H_4-**B** and their double- and triple-stranded dinuclear complexes.

The formation of triple-stranded, dinuclear helicates or *meso* complexes based on catechol-containing ligands is well documented. Much less is known about ligands with benzene-*o*-dithiol donor functions. In this study, we describe the coordination chemistry of bis(benzene-*o*-dithiol) ligands H_4-**3** and H_4-**8** (Scheme 2). Both ligands form dinuclear triple-stranded complexes with Ti^{4+} (Scheme 3). For the symmetrical ligand H_4-**3**, we observe formation of three isomeric dinuclear complexes (*meso* complexes $(Ph_4As)_4$[**9**] and $(Et_4N)_4$[**10**] and the helicate $(Bu_4N)_4$[**11**]). Molecular-modeling calculations were performed on these complexes to elucidate the reasons for the formation of *meso* complexes versus helicates. With the synthesis of the directional ligand H_4-**8** we succeeded in the preparation of a new type of bis(benzene-*o*-dithiol) ligand by linkage of the two differently functionalized benzene-*o*-dithiol groups **1** and **6** (Scheme 2). Ligand H_4-**8** reacts with Ti^{4+} to form dinuclear, triple-stranded complexes that exhibit either a parallel or an antiparallel orientation of the ligand strands.

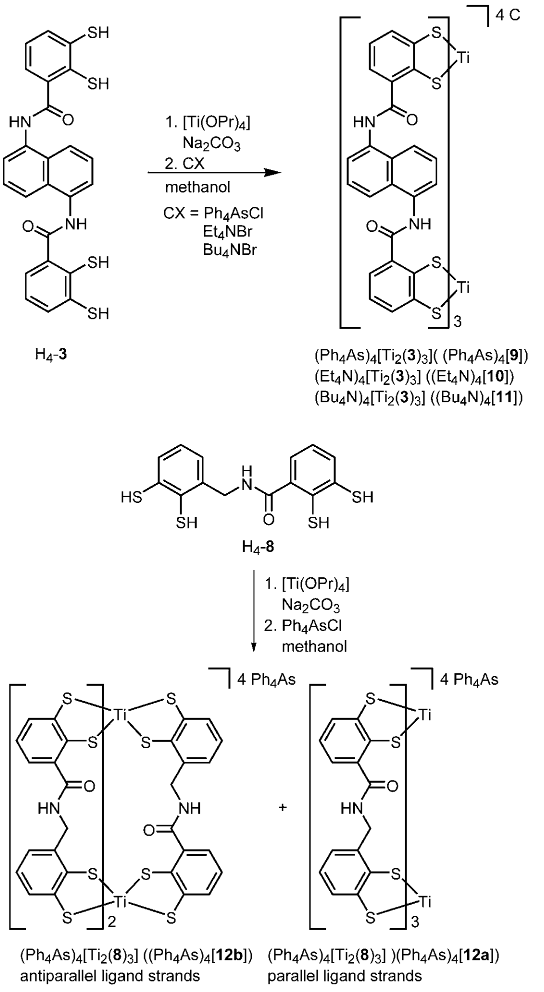


Scheme 2. Preparation of the 1,5-diamidonaphthalene-bridged ligand H_4-**3** (top) and the unsymmetrically bridged ligand H_4-**8** (bottom).

Results and Discussion

Synthesis of ligands H_4-3 and H_4-8: Scheme 2 (top) depicts the preparation of the 1,5-diamidonaphthalene-bridged bis(benzene-*o*-dithiol) ligand H_4-**3**. The synthesis starts with 2,3-di(isopropylmercapto)benzoic acid chloride (**1**), which was prepared as previously described.[9] Reaction of **1** and 1,5-diaminonaphthalene in the presence of NEt_3 gave the S-alkylated ligand precursor **2**. The isopropyl protection groups were removed by treatment of **2** with sodium and naphthalene in THF[9] to give the air-sensitive ligand H_4-**3** after hydrolysis with HCl/H_2O.[16]

The unsymmetrical ligand H_4-**8** was obtained from the acid chloride derivative **1** and benzylamine **6**. This latter



Scheme 3. Formation of dinuclear complexes derived from ligand H$_4$-**3** and H$_4$-**8**.

building block was prepared by a Gabriel synthesis starting with 2,3-di(isopropylmercapto)benzoyl bromide (**4**).[9b,c] Compound **4** reacts with potassium phthalimide to form the phthalimide derivative **5**, which upon reaction with hydrochloric acid and after basic workup yields 2,3-di(isopropylmercapto)benzoyl amine (**6**). One equivalent each of **6** and **1** can be coupled to give the ligand precursor **7**, which after reductive cleavage of the S-*i*Pr bonds yields ligand H$_4$-**8**. Since most bis(benzene-*o*-dithiol) ligands are only soluble in DMF, ligands H$_4$-**3** and H$_4$-**8** can be purified by washing the crude reaction products with water and diethyl ether.

Synthesis of dinuclear, triple-stranded complexes: Ligand H$_4$-**3** reacts with Ti^{4+} ions in methanol in the presence of Na$_2$CO$_3$ as a base, to form a deep red solution (λ_{max}= 540 nm), typical for the $\{Ti(bdt)_3\}^{2-}$ chromophore.[17] It is reasonable to assume that the triple-stranded dinuclear complex Na$_4$[Ti$_2$(**3**)$_3$] is formed through a self-assembly reaction.[16] In the presence of Li$_2$CO$_3$ or K$_2$CO$_3$ instead of Na$_2$CO$_3$, the corresponding complexes Li$_4$[Ti$_2$(**3**)$_3$] and K$_4$[Ti$_2$(**3**)$_3$] were obtained, indicating no influence of the type of alkali metal cation on the composition of the assembled complex anion. However, none of the complexes M$_4$[Ti$_2$(**3**)$_3$] (M = Li$^+$, Na$^+$, K$^+$) could be isolated in an analytically pure form. Therefore, the alkali metal cations were exchanged for larger organic cations. The use of these cations allowed the isolation of the salts (Ph$_4$As)$_4$[**9**], (Et$_4$N)$_4$[**10**],[16] and (Bu$_4$N)$_4$[**11**] (Scheme 3) in an analytically pure form and in yields of 40–60 % after recrystallization from DMF/acetonitrile/diethyl ether. The compositions of the salts were confirmed by elemental analyses and ESI mass spectroscopy.

The unsymmetrical ligand H$_4$-**8** was reacted with [Ti(OPr)$_4$] under the same conditions as those described for ligand H$_4$-**3** (Scheme 3) leading to the triple-stranded dinuclear complex (Ph$_4$As)$_4$[Ti$_2$(**8**)$_3$] ((Ph$_4$As)$_4$[**12**]). Due to the directionality of the ligand, several different stereoisomers of the anion [**12**]$^{4-}$ can form in this reaction. Figure 1 shows the possible stereoisomers. Both the parallel and the antiparallel orientation of the ligand strands each lead to a pair of helical enantiomers. Two more pairs of enantiomers result for the nonhelical complexes with the parallel or the antiparallel orientation of the ligand strands. Thus a total of eight stereoisomers exist for anions of type [Ti$_2$(**8**)$_3$]$^{4-}$.

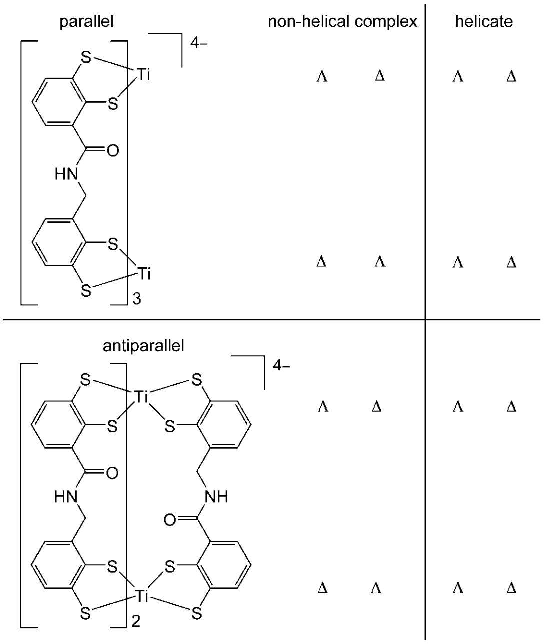


Figure 1. Possible stereoisomers formed with ligand H$_4$-**8** and Ti^{4+}.

X-ray diffraction analyses: We have briefly described the molecular structures of (Ph$_4$As)$_4$[**9**]·2 Et$_2$O and (Et$_4$N)$_4$[**10**]·2 DMF·H$_2$O.[16] In an extension of this study and for comparison we describe here the molecular structure of the salt (Bu$_4$N)$_4$[**11**], which also contains the dinuclear triple-stranded tetraanion [Ti$_2$(**3**)$_3$]$^{4-}$. Although the three dinuclear, triple-stranded complex anions [**9**]$^{4-}$–[**11**]$^{4-}$ have identical formulae ([Ti$_2$(**3**)$_3$]$^{4-}$; Scheme 3) they exhibit different molecular structures that appear to be caused by the differences in the countercations.

Both anions $[\mathbf{9}]^{4-}$ and $[\mathbf{10}]^{4-}$ are *meso* complexes with opposite absolute configurations of the metal centers (Λ and Δ). Complex anion $[\mathbf{9}]^{4-}$ crystallized in the centrosymmetric space group $P2_1/n$ with the tetraanion residing on a crystallographic inversion center located at the midpoint of the C26−C26* bond (Figure 2, left). The titanium atoms are coordinated by six sulfur atoms in a strongly distorted octahedral fashion with a calculated twist angle of $\phi=29.7^\circ$. The view along the Ti–Ti axis (Figure 2, right) shows the centrosymmetric geometry of anion $[\mathbf{9}]^{4-}$. The naphthalene spacers of two ligand strands adopt a parallel arrangement. The third ligand strand proceeds from one metal ion to the other, crossing the Ti–Ti axis.

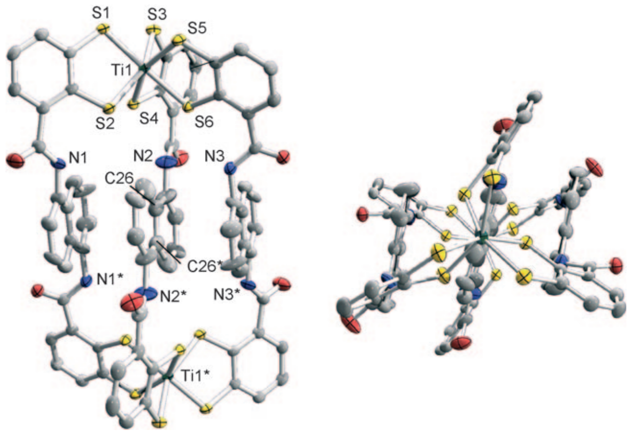


Figure 2. Molecular structure of the complex anion $[\mathbf{9}]^{4-}$ as seen from a side view (left) and along the Ti–Ti axis (right). Hydrogen atoms, cations, and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti−S1 2.423(2), Ti−S2 2.422(2), Ti−S3 2.427(2), Ti−S4 2.410(2), Ti−S5 2.419(2), Ti−S6 2.404(2); S1-Ti-S2 80.87(5), S3-Ti-S4 80.19(5), S5-Ti-S6 97.95(5).

Exchange of the $\mathrm{Ph_4As^+}$ cations in $(\mathrm{Ph_4As})_4[\mathbf{9}]$ for $\mathrm{Et_4N^+}$ cations gave compound $(\mathrm{Et_4N})_4[\mathbf{10}]$ (Scheme 3). The X-ray diffraction study revealed formation of the salt $(\mathrm{Et_4N})_3[\mathrm{Et_4N}\subset\mathrm{Ti_2}(\mathbf{3})_3]$ containing the anion $[\mathrm{Et_4N}\subset\mathrm{Ti_2}(\mathbf{3})_3]^{3-}$ with one tetraethylammonium cation located between the two metal atoms. The two titanium atoms in the complex anion are each coordinated by three benzene-*o*-dithiolato groups differing slightly in their coordination geometry and exhibiting opposite chiralities (Ti1: Δ, $\phi=24.0^\circ$; Ti2: Λ, $\phi=30.9^\circ$). This leads again to the formation of the *meso* complex. The tetraethylammonium cation located between two ligand strands forces the three ligands to adopt slightly different orientations (Figure 3).

Related bond parameters in the $[\mathrm{Et_4N}\subset\mathrm{Ti_2}(\mathbf{3})_3]^{3-}$ anion are similar to those found for the $[\mathrm{Ti_2}(\mathbf{3})_3]^{4-}$ anion. Long and variable N···S separations (ranging from 2.981 to 4.132 Å) rule out the presence of N−H···S hydrogen bonds. The $\mathrm{TiS_2C_4H_4}$ fragments in both $[\mathrm{Ti_2}(\mathbf{3})_3]^{4-}$ and $[\mathrm{Et_4N}\subset\mathrm{Ti_2}(\mathbf{3})_3]^{3-}$ are bent about the S···S vector in accord with previous observations.[10–11,17–18]

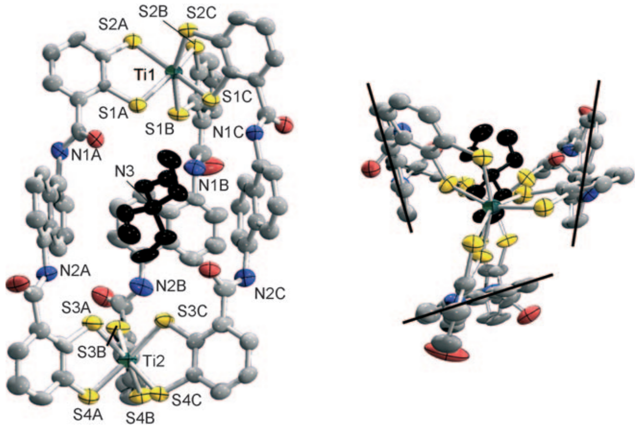


Figure 3. Molecular structure of the complex anion $[\mathrm{Et_4N}\subset\mathrm{Ti_2}(\mathbf{3})_3]^{3-}$ as seen from a side view (left) and along the Ti–Ti axis (right). The tetraethylammonium cation is drawn in black. Additional cations, solvent molecules, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1−S1A 2.397(3), Ti1−S1B 2.381(3), Ti1−S1C 2.403(4), Ti1−S2A 2.453(3), Ti1−S2B 2.439(3), Ti1−S2C 2.436(3), Ti2−S3A 2.380(3), Ti2−S3B 2.407(3), Ti2−S3C 2.381(4), Ti2−S4A 2.446(3), Ti2−S4B 2.430(3), Ti2−S4C 2.459(4); S1A-Ti1-S2A 80.70(11), S1B-Ti1-S2B 82.11(10), S1C-Ti1-S2C 81.52(11), S3A-Ti2-S4A 81.12(11), S3B-Ti2-S4B 81.00(11), S3C-Ti2-S4C 80.12(13).

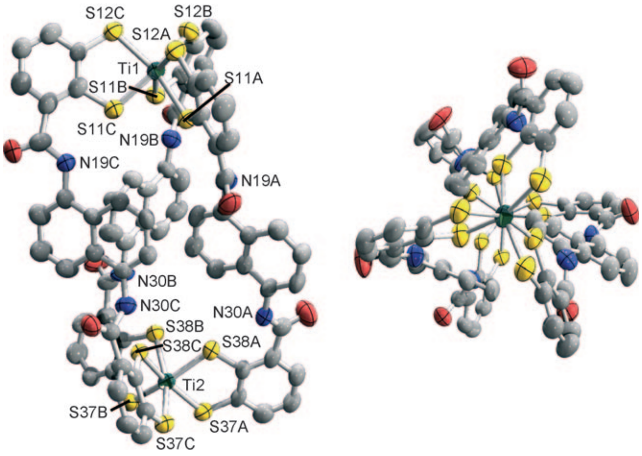


Figure 4. Molecular structure of the complex anion $[\mathbf{11}]^{4-}$ shown parallel (left) and perpendicular (right) to the Ti–Ti axis. Hydrogen atoms and cations have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1−S11A 2.412(2), Ti1−S11B 2.426(3), Ti1−S11C 2.411(2), Ti1−S12A 2.399(3), Ti1−S12B 2.406(3), Ti1−S12C 2.395(2), Ti2−S37A 2.397(2), Ti2−S37B 2.407(2), Ti2−S37C 2.365(2), Ti2−S38A 2.426(2), Ti2−S38B 2.426(2), Ti2−S38C 2.441(2); S11A-Ti1-S12A 81.07(8), S11B-Ti1-S12B 81.29(9), S11C-Ti1-S12C 81.21(8), S37A-Ti2-S38A 80.62(8), S37B-Ti2-S38B 81.32(8), S37C-Ti2-S38C 81.17(8).

A third geometry for the anion $[\mathrm{Ti_2}(\mathbf{3})_3]^{4-}$ was found in compound $(\mathrm{Bu_4N})_4[\mathrm{Ti_2}(\mathbf{3})_3]$ ($(\mathrm{Bu_4N})_4[\mathbf{11}]$). Figure 4 shows the molecular structure of the complex anion both parallel (left) and perpendicular to the Ti–Ti axis (right). Each titanium atom is surrounded by six sulfur atoms in a strongly distorted octahedral fashion with calculated twist angles of 40.0 (Ti1) and 35.2° (Ti2). Surprisingly in this case, both titanium atoms possess the same absolute configuration, Λ, and therefore tetraanion $[\mathbf{11}]^{4-}$ is a dinuclear, triple-stranded helicate with a calculated helix angle of 58.2°. Since $(\mathrm{Bu_4N})_4[\mathbf{11}]$ crystallized in the centrosymmetric space group

$C2/c$ both the Λ,Λ and the Δ,Δ enantiomers are present in the same crystal. Complex anion $[\mathbf{11}]^{4-}$ shows nonbonding N···S separations in the range of 2.904–3.017 Å, indicative of the presence of only weak intramolecular N–H···S hydrogen bonds. The assumption of only weak hydrogen bonds is corroborated by the observation of Ti–S_{ortho} bonds that are not significantly longer than the Ti–S_{meta} bonds. A significant difference in the Ti–S bond lengths would have been expected in the case of the formation of strong N–H···S_{ortho} hydrogen bonds.[11] A comparison of the molecular structure of the helical $(Bu_4N)_4[\mathbf{11}]$ to both *meso* complexes $(Ph_4As)_4[\mathbf{9}]$ and $(Et_4N)_4[\mathbf{10}]$ revealed similar Ti–S bond lengths and S-Ti-S bite angles. Since only the size of the counterions varies in the three compounds, this is most likely responsible for the structural differences, with the encapsulated tetraethyl ammonium cation accounting for the structural differences between the two *meso* complexes $[\mathbf{9}]^{4-}$ and $[\mathbf{10}]^{4-}$.

The influence of the counterions on the coordination geometry of mononuclear tungsten and molybdenum complexes of type $[M(bdt)_3]^{n-}$ has been studied by Sugimoto and co-workers.[19] They observed a dependence of the coordination geometry around the metal center from the counterion employed in the reaction.

The factors that govern the preferred formation of either the *meso* complex or the helicate have been discussed by Albrecht and co-workers.[20] Experimental studies performed on complexes with alkyl-bridged dicatecholato ligands revealed the formation of helicates with an even number of methylene groups in the alkyl spacer and *meso* complexes with an odd number of methylene groups in the spacer. Albrecht also described a spontaneous self-assembly process in which the formation of a dinuclear triple-stranded tetraanionic *meso* complex with dicatecholato ligands is influenced by the counterion present.[20b] In general, however, there are very few examples of ligands forming different isomers in metal-directed self-assembly reactions as observed for the anions $[\mathbf{9}]^{4-}$–$[\mathbf{11}]^{4-}$.[2b]

NMR spectroscopy studies: The observed differences in the molecular structures of the dinuclear anions $[\mathbf{9}]^{4-}$–$[\mathbf{11}]^{4-}$ in the solid state have also been studied in solution by NMR spectroscopy. The anions in $(Ph_4As)_4[\mathbf{9}]$ and $(Et_4N)_4[\mathbf{10}]$ exhibit quite simple ^1H NMR spectra with only one set of signals for the protons of all three ligand strands indicative of C_3 symmetry of the complex anions in solution. The simple NMR spectra are also an indication of the formation of only one pair of enantiomers, either *meso* complexes or helicates in solution (Figure 1).

For both anions $[\mathbf{9}]^{4-}$ and $[\mathbf{10}]^{4-}$, the signals for the aromatic protons of the benzene-*o*-dithiolato groups appear as two doublet of doublets and a triplet, typical for an AMX spin system. The molecular-structure analysis of $(Et_4N)_4[\mathbf{10}]$ revealed the presence of an encapsulated tetraethyl ammonium cation located in between the titanium atoms in a triple-stranded *meso* complex (Figure 3). The ^1H NMR spectrum of the complex recorded at ambient temperature (Figure 5), however, showed only one set of resonances for all four tetraethylammonium cations. We therefore assume that the tetraethylammonium exchange is fast compared to the NMR spectroscopy timescale. The resonance for the amide protons in complexes $(Ph_4As)_4[\mathbf{9}]$ and $(Et_4N)_4[\mathbf{10}]$ is shifted downfield relative to the free ligand H_4-**3** ($\Delta\delta = 0.75$ and 0.62 ppm in $[\mathbf{9}]^{4-}$ and $[\mathbf{10}]^{4-}$, respectively). We have previously noted a similar downfield shift for related dinuclear, triple-stranded complexes with bis(benzene-*o*-dithiolato) ligands and assign this shift to the formation of intramolecular N–H···S hydrogen bonds in solution.[10,11] These hydrogen bonds, however, have not been detected in the solid-state molecular structures of the complex anions $[\mathbf{9}]^{4-}$ and $[\mathbf{10}]^{4-}$.

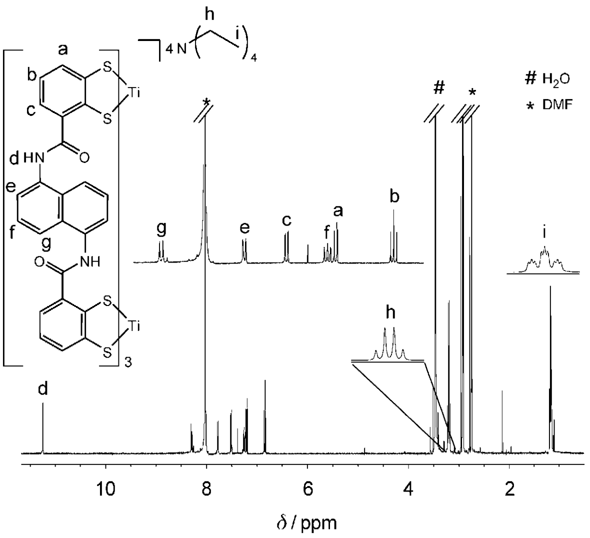


Figure 5. ^1H NMR spectrum of complex $(Et_4N)_4[\mathbf{10}]$ at ambient temperature in $[D_7]$DMF.

Even at low temperature (213 K) the ^1H NMR spectroscopy resonances for the protons of the tetraethylammonium cations in $(Et_4N)_4[\mathbf{10}]$ were only recorded as broad signals. Since the molecular-structure determination of $(Et_4N)_4[\mathbf{10}]$ revealed one encapsulated tetraethylammonium cation in the solid state (Figure 3), two sets of resonances in a ratio of 3:1 for the free and the encapsulated tetraethyl ammonium cations were expected at low temperature where the exchange between free and encapsulated tetraethyl ammonium cations should be slowed down. Figure S1 (see the Supporting Information) shows, however, that only one set of resonances at $\delta \approx 1.2$ and 3.2 ppm was detected over a wide temperature range including the lowest data-collection temperature (213 K). We assume that at ambient temperature a fast exchange of the encapsulated tetraethylammonium cation with nonencapsulated cations occurs, whereas at low temperature all tetraethylammonium cations remain outside of the complex and no interaction with the anion $[\mathbf{10}]^{4-}$ takes place at all.

The proton NMR spectrum of compound $(Bu_4N)_4[Ti_2(\mathbf{3})_3]$ ($(Bu_4N)_4[\mathbf{11}]$; Figure 6) shows the presence of two isomers in solution. Presumably these are a helical and a *meso* complex, while only one set of resonances was observed for the tetrabutylammonium cations. For the helical anion, the reso-

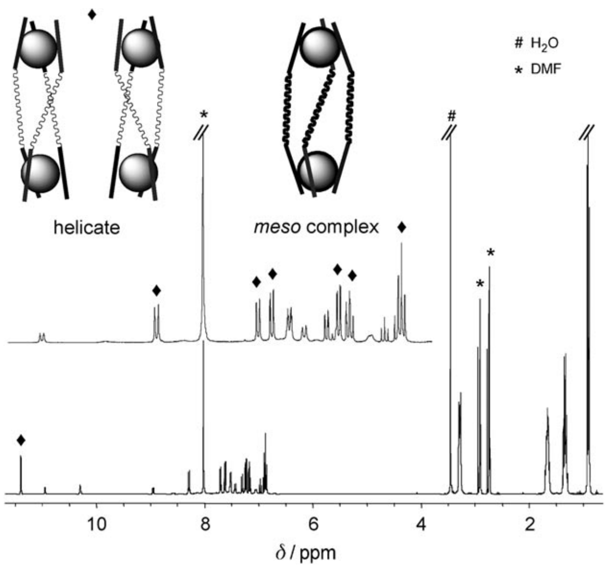


Figure 6. ^{1}H NMR spectrum of complex $(Bu_4N)_4$[**11**] at ambient temperature in [D$_7$]DMF. Resonances for the helical isomer are marked with ◆.

nance for the amide protons ($\delta = 11.40$ ppm) is shifted downfield relative to the resonance for the free ligand H$_4$-**3** ($\Delta\delta = 0.77$ ppm), which is indicative of N−H···S hydrogen bonds in solution. Contrary to this situation, two resonances for the amide protons were detected for the *meso* complex at $\delta = 10.29$ and 10.94 ppm, respectively, in a ratio of 2:1, shifted upfield and downfield relative to the resonance for the free ligand. Figure 6 illustrates that two types of ligand strands exist in a *meso* complex that accounts for the two observed amide resonances in a ratio of 2:1.

The ^{1}H NMR spectrum of $(Bu_4N)_4$[**11**] also displays the typical signals for the aromatic protons of an AMX spin system for both isomeric complexes. One set of signals was detected for the three ligand strands of the helical anion (these are marked with ◆ in Figure 6). The *meso* stereoisomer, however, leads to two sets of Ar−H resonances in a ratio of 2:1. Although some of the resonances for the *meso* complex are obscured by additional resonances in Figure 6, the full set of resonances was identified by 2D NMR spectroscopy experiments that verified the presence of the two isomers in solution. Since both isomeric species are present in solution at ambient temperature, we expect a small energy difference between them. However, up to a measuring temperature of 390 K the spectra do not simplify, which suggests a high barrier and consequently a low rate for interconversion.

The ^{1}H NMR spectrum of ligand H$_4$-**8** showed, as expected, two doublet of doublets and one triplet for the protons of each of the two aromatic rings. A doublet was detected at $\delta = 4.67$ ppm for the methylene protons coupled to the amide proton at $\delta = 9.07$ ppm (triplet). The broad signal at $\delta = 5.49$ ppm for the resonances of the sulfur protons disappears upon deprotonation and reaction with Ti^{4+}.

Figure 7 displays the ^{1}H NMR spectrum of the mixture of complexes $(Ph_4As)_4$[**12a**] and $(Ph_4As)_4$[**12b**] (Scheme 3) measured at ambient temperature and at 370 K in [D$_7$]DMF. At ambient temperature the spectrum reveals only two sharp signals for the amide protons in a ratio of 3:2 at $\delta =$ 10.17 and 10.10 ppm, respectively. A third very broad signal was detected at $\delta = 9.81$ ppm. These resonances can be assigned to a complex anion with three ligand strands in a parallel orientation ($\delta = 10.17$ ppm) and a complex anion with an antiparallel orientation of the ligand stands ($\delta = 10.10$ und 9.81 ppm) occurring in about equal amounts in solution. At higher temperature (370 K) the spectrum shows three sharp amide-H resonances in a ratio of 3:2:4 and more signals for the aromatic protons. This would indicate an excess of the complex anion [**12b**]$^{4-}$ with the antiparallel orientation of the ligand strands at elevated temperature.

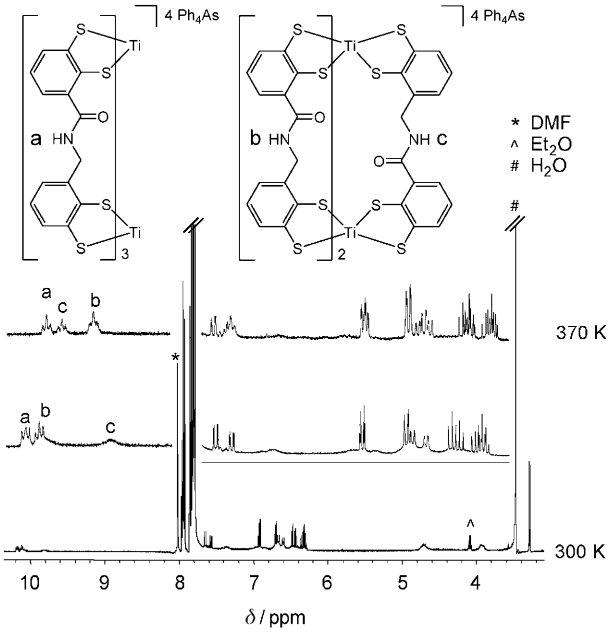


Figure 7. ^{1}H NMR spectrum of complex $(Ph_4As)_4$[**12**] (resonances for both isomers [**12a**]$^{4-}$ and [**12b**]$^{4-}$ are detectable) at ambient temperature and 370 K in [D$_7$]DMF.

For both isomers [**12a**]$^{4-}$ and [**12b**]$^{4-}$ the signals for the amide protons are shifted downfield relative to the free ligand, indicative of the formation of N−H···S hydrogen bonds in solution. In addition, the ^{1}H NMR spectrum displays two signals for the diastereotopic hydrogen atoms of the methylene groups at $\delta = 4.67$ and 3.90 ppm. We consider the observation of three signals for the amide protons as indication for the formation of two stereoisomers in solution, one with a parallel and the other one with an antiparallel orientation of the ligand strands. Supplementary 2D NMR spectroscopy experiments support this assumption. The question as to whether the isomer with the parallel orientation is a *meso* complex or a helicate must remain unanswered at this time.

Molecular-modeling calculations: In the reaction of ligand H$_4$-**3** with Ti^{4+} we observed formation of three complex anions with differing structural properties. Both *meso*-complex anions ($[\mathbf{9}]^{4-}$ and $[\mathbf{10}]^{4-}$) as well as helicate $[\mathbf{11}]^{4-}$ have been characterized by X-ray diffraction studies in the solid state. Both metal centers in the helical anion $[\mathbf{11}]^{4-}$ possess the same absolute configuration (Λ,Λ or Δ,Δ), whereas the metal centers in the *meso* complex anions exhibit opposite absolute configurations. Based on the observation of complex anions with different absolute configurations generated from the same metal ion/ligand combination we became interested in the magnitude of the barrier for interconversion of these isomers and addressed this question with DFT calculations.

Since transition-state searches with complexes consisting of about 140 atoms are beyond our means, we reduced the system to a smaller representative unit, the mononuclear titanium tris(benzene-*o*-dithiolato) complex $[Ti(bdt)_3]^{2-}$. Geometry optimization of this complex with DFT using the B3LYP functional[21] and the SDD basis set[22] gave the expected distorted octahedral species as a global minimum. The octahedral form is energetically favored over the D_{3h} and C_{3h} symmetrical trigonal-prismatic ones (Figure 8). Raymond and co-workers demonstrated earlier for mononuclear catecholato complexes $[Ti(cat)_3]^{2-}$ (cat = catecholato dianion) that the D_{3h} form is the transition structure for interconversion of a Λ isomer to its Δ enantiomer.[23a]

Figure 8. B3LYP/SDD-optimized geometries for the pseudo-O_h (left), C_{3h} (middle), and D_{3h} configurations (right) of $[Ti(bdt)_3]^{2-}$.

Contrary to the situation found for the $[Ti(cat)_3]^{2-}$ case, in the present study on $[Ti(bdt)_3]^{2-}$ we found the D_{3h} symmetrical structure to have a higher-order saddle point with two (degenerate) imaginary frequencies. Instead, the C_{3h} symmetrical structure represents the transition state for the Λ→Δ interconversion with a single imaginary frequency (Figure 8). The relative energies given in Table 1 together with the two for $[Ti(cat)_3]^{2-}$ show indeed a smaller activation energy for the Λ→Δ interconversion of the $[Ti(bdt)_3]^{2-}$ isomers (6.6 kcal mol^{-1}), as compared with that for the catecholato analogue (10.2 kcal mol^{-1}).

Table 1. Relative energies (in kcal mol^{-1}) for the B3LYP/SDD-optimized structures of mononuclear tris(benzene-*o*-dithiolato) and tricatecholato titanium complexes.

Complex	D_3	D_{3h}	C_{3h}
$[Ti(bdt)_3]^{2-}$	0	15.1 [b]	6.6 [a]
$[Ti(cat)_3]^{2-}$	0	10.2 [a]	–[c]

[a] One and [b] two (degenerate) imaginary frequencies. [c] Optimization of the C_{3h}-symmetric tris(catecholato) resulted in all cases in the D_{3h}-symmetric isomer.

The origin of the difference in transition structures must be sought in the different nature of the donor groups. Titanium–oxygen bonds are usually short and the M–catecholato rings in such complexes are likely to be planar, which is the case for $[Ti(cat)_3]^{2-}$. Their interconversion proceeds via the Bailar transition state[23b] as expected for pseudo-octahedral complexes with three chelating ligands. This behavior is different in the case of bdt^{2-} ligands due to the longer Ti–S bond lengths caused by the softer nature of the sulfur donor. In the C_{3h} transition structure of complex $[Ti(bdt)_3]^{2-}$, the repulsion between the sulfur lone pairs is minimized by the bent arrangement of the ligands.[10–11,17–18]

Next, based on the X-ray molecular structure of $[\mathbf{9}]^{4-}$, we optimized its geometry at B3LYP/SDD, and the results for the optimized structure $[\mathbf{9a}]^{4-}$ are depicted in Figure 9 ($[\mathbf{9a}]^{4-}$, left) with selected bond lengths and angles summarized in Table 2. The slightly longer bond lengths for the calculated structure may be due to the absence of the counterions and solvent molecules in the geometry optimization.

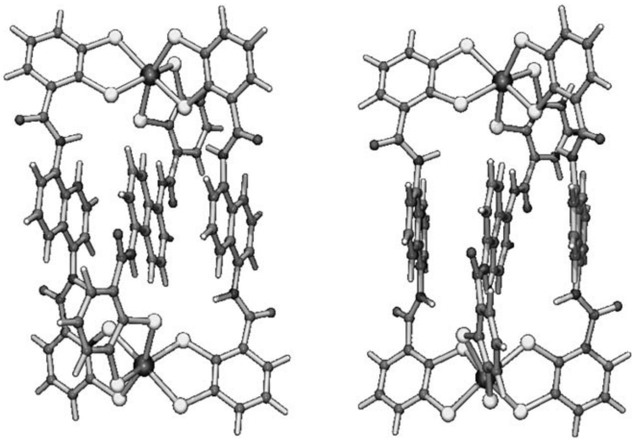


Figure 9. B3LYP/SDD-optimized structures for the *meso* complex anion $[\mathbf{9a}]^{4-}$ (left) and the corresponding helicate $[\mathbf{9b}]^{4-}$ (right).

Table 2. Characteristic bond lengths [Å] and angles [°] for $[\mathbf{9}]^{4-}$ obtained from the X-ray diffraction study and those obtained at B3LYP/SDD for the *meso* complex ($[\mathbf{9a}]^{4-}$) and helicate ($[\mathbf{9b}]^{4-}$) complex anions.

Bond lengths and angles	$[\mathbf{9}]^{4-}$ (X-ray data)	$[\mathbf{9a}]^{4-}$ (*meso* complex)	$[\mathbf{9b}]^{4-}$ (helicate)
$Ti-S_{ortho}$	2.403–2.422	2.438–2.490	2.420–2.480
$Ti-S_{meta}$	2.419–2.427	2.420–2.470	2.420–2.470
N···S	3.026–3.043	3.090–3.170	3.050–3.190
H-N-C-O[a]	174.13	175.37	176.26
S_o-Ti-S_m[b]	80.33	81.28	81.43

[a] Average dihedral angle. [b] Average bite angle.

In the next step we changed the absolute configurations of the titanium centers from Λ,Δ in the *meso* complex $[\mathbf{9a}]^{4-}$ (Figure 9, left) to Λ,Λ in the helicate $[\mathbf{9b}]^{4-}$ (Figure 9, right). More specifically, the Δ ("bottom") titanium unit in $[\mathbf{9a}]^{4-}$ was changed manually to the Λ configuration and the resulting structure was optimized. Interestingly, the energy difference between the two isomers amounts to only 0.68 kcal mol^{-1}. Hence, this small energy difference together with the discussed low barrier for Λ,Δ interconversion, explains the observed formation of both the *meso* complexes and helicate with ligand H$_4$-**3**.

Conclusion

We have presented a detailed investigation of the coordination chemistry of the naphthalene-bridged bis(benzene-*o*-dithiol) ligand H$_4$-**3**. The interaction of the hard titanium cation with the soft sulfur donors of the noninnocent bdt^{2-} ligand leads to new structural motifs compared with the analogous catecholato ligand. Ligand H$_4$-**3** is the first bis(benzene-*o*-dithiolato) derivative that has been shown to be capable of forming isomeric complexes (*meso* complexes and helicate) in metal-directed self-assembly reactions with Ti^{4+}. Both a helicate and a *meso* complex with the composition (Bu$_4$N)$_4$[Ti$_2$(**3**)$_3$] were detected in solution by ^{1}H NMR spectroscopy, whereas only the helicate could be crystallized from such solutions. Only one *meso* complex anion was detected in the solid state by using X-ray diffraction and in solution by ^{1}H NMR spectroscopy for the compounds (Ph$_4$As)$_4$[Ti$_2$(**3**)$_3$] and (Et$_4$N)$_4$[Ti$_2$(**3**)$_3$]. The formation of isomeric complex anions [Ti$_2$(**3**)$_3$]$^{4-}$ is most likely caused by the different cations present during their synthesis. Analysis with density functional theory showed different mechanisms for the Λ→Δ interconversion of tris(catecholato) and tris(benzene-*o*-dithiolato) titanium complexes. The Λ→Δ interconversion of the mononuclear [Ti(bdt)$_3$]$^{2-}$ complex proceeds via a C_{3h}-symmetric transition structure, whereas a D_{3h} transition state was previously found for the [Ti(cat)$_3$]$^{4-}$ complex anion. The DFT calculations also revealed a small activation energy for the Λ→Δ interconversion, which would transform a *meso* complex anion of type [Ti$_2$(**3**)]$^{4-}$ into the helicate.

Finally, we described the synthesis and coordination chemistry of the unsymmetrical bis(benzene-*o*-dithiol) ligand H$_4$-**8**. The topology of the ligand provides two electronically different donor units, one being more electron rich than the other. The self-assembly reactions of ligand H$_4$-**8** with Ti^{4+} lead to a mixture of dinuclear triple-stranded complexes exhibiting either a parallel or an antiparallel orientation of the ligand stands.

Experimental Section

Computational methods: All density functional theory calculations (B3LYP)[21] were performed with the Gaussian 03 suite of programs,[24] using the SDD basis set and pseudopotentials for titanium[22] and the D95V[25] basis set for all other atoms. The nature of the transition-state structures was confirmed by frequency calculations.

Syntheses and analyses: All operations were carried out under an atmosphere of dry argon using Schlenk and vacuum techniques. Solvents were dried by standard methods and freshly distilled prior to use. NMR spectra were recorded at 298 K with Bruker AC 200 (200 MHz), Bruker AMX 400 (400 MHz), or Varian Inova (600 MHz) spectrometers and are reported relative to TMS as an internal standard or to the solvent signal. IR spectra were measured with a Bruker Vector 22 IR spectrometer. Mass spectra were obtained with Varian MAT 212 (EI), Micromass Quattro LC-Z (ESI), or Bruker Reflex IV (MALDI) spectrometers. Elemental analyses were performed with a Vario EL III CHNS analyzer. Commercially available [Ti(OPr)$_4$] (Aldrich) was used without further purification. 2,3-Di(isopropylmercapto)benzoic acid chloride (**1**)[9a,c] and 2,3-di(isopropylmercapto)benzoyl bromide (**4**)[9b,c] were prepared as described previously.

1,5-Bis[2,3-di(isopropylmercapto)benzamido]naphthalene (2): Freshly prepared 2,3-di(isopropylmercapto)benzoic acid chloride (**1**; 653 mg, 2.26 mmol) was dissolved in THF (20 mL) and this solution was added to a solution of 1,5-diaminonaphthalene (179 mg, 1.13 mmol) and NEt$_3$ (1.7 mmol) in THF (40 mL). The reaction mixture was stirred for 12 h at ambient temperature. Subsequently, insoluble material was removed by filtration and the solvent was removed from the filtrate under vacuum. The solid residue was purified by column chromatography (silica gel, CH$_2$Cl$_2$/*n*-hexane 1:1, v/v). Yield: 710 mg (1.07 mmol, 95 %); ^{1}H NMR (400 MHz, [D$_7$]DMF): $\delta = 10.39$ (s, 2 H; N-H), 8.23 (d, ^3J(H,H) = 8.4 Hz, 2 H; naphthalene-H), 7.70 (d, ^3J(H,H) = 8.4 Hz, 2 H; naphthalene-H), 7.58 (t, ^3J(H,H) = 8.4 Hz, 2 H; naphthalene-H), 7.48 (t, ^3J(H,H) = 6.7 Hz, 2 H; Ar-H), 7.37 (dd, ^3J(H,H) = 6.7 Hz, ^4J(H,H) = 2.4 Hz, 2 H; Ar-H), 7.19 (dd, ^3J(H,H) = 6.7 Hz, ^4J(H,H) = 2.4 Hz, 2 H; Ar-H), 3.60 (m, 4 H; C*H*-(CH$_3$)$_2$), 1.36 (d, 6 H; CH$_3$), 1.19 ppm (d, 6 H; CH$_3$); ^{13}C NMR (100 MHz, [D$_7$]DMF): $\delta = 167.7$ (C(O)NH), 144.8, 142.5 (C-S), 133.7, 129.6, 125.1, 122.9, 121.7 (naphthalene-C), 129.1, 127.2, 126.7, 123.0 (Ar-C), 45.7, 34.8 (*C*H(CH$_3$)$_2$), 25.0, 23.0, 22.7, 22.4 ppm (CH$_3$); elemental analysis calcd (%) for C$_{36}$H$_{42}$N$_2$O$_2$S$_4$: C 65.22, H 6.39, N 4.23, S 19.34; found: C 65.28, H 6.29, N 4.01, S 18.18.

Ligand H$_4$-3: Dry, freshly distilled THF (60 mL) was added to a mixture of compound **2** (710 mg, 1.07 mmol), sodium (247 mg, 10.7 mmol), and naphthalene (697 mg, 5.35 mmol). The reaction mixture was stirred for 12 h. Subsequently methanol (10 mL) was added to remove unreacted sodium. All solvents were then removed under vacuum and the solid residue was dissolved in degassed water and washed three times with degassed diethyl ether (20 mL each). Insoluble material was removed by filtration. The clear aqueous solution was treated dropwise with HCl (37 %) until a white precipitate formed. The precipitate was isolated by filtration and washed with water and diethyl ether. The solid residue was dried under vacuum. Yield: 450 mg (0.91 mmol, 85 %); ^{1}H NMR (400 MHz, [D$_7$]DMF): $\delta = 10.63$ (s, 2 H; N-H), 8.26 (m, 2 H; naphthalene-H), 7.93 (m, 2 H; Ar-H), 7.70 (m, 2 H; naphthalene-H), 7.62 (m, 2 H; Ar-H), 7.49 (t, 2 H; Ar-H), 7.25 (t, 2 H; naphthalene-H), 3.95 ppm (br s, 4 H; S-H). ^{13}C NMR data could not be obtained due to the instability of the ligand in solution over longer periods of time.[16]

2,3-Di(isopropylmercapto)benzoyl phthalimide (5): 2,3-Di(isopropylmercapto)benzoyl bromide (**4**; 1.36 g, 4.26 mmol) and potassium phthalimide (1.18 g, 6.37 mmol) were dissolved in acetone (50 mL). The reaction mixture was heated under reflux for 12 h. Solids were isolated by filtration and suspended in water (40 mL). The aqueous suspension was heated under reflux for two more hours. The reaction mixture was then filtered and the solid residue was washed with water, recrystallized from ethanol, and dried under vacuum. Compound **5** was isolated as a white crystalline solid (1.36 g, 3.53 mmol, 83 %). ^{1}H NMR (400 MHz, [D$_7$]DMF): $\delta = 7.88$ (d, 2 H; phthalimide-H), 7.74 (d, 2 H; phthalimide-H), 7.17 (t, 1 H; Ar-H), 7.16 (d, 1 H; Ar-H), 6.81 (d, 1 H; Ar-H), 5.21 (d, 2 H; CH$_2$), 3.56 (sept, 1 H; C*H*(CH$_3$)$_2$), 3.48 (sept, 1 H; C*H*(CH$_3$)$_2$), 1.38 (d, 6 H; CH$_3$), 1.32 ppm (d, 6 H; CH$_3$); ^{13}C NMR (100 MHz, [D$_7$]DMF): $\delta = 168.1$ (C(O)N), 145.8, 130.7 (C-S), 141.5, 134.1, 132.2, 129.0, 125.5, 123.4, 122.3 (Ar-C), 41.0 (CH$_2$), 39.4, 35.9 (CH), 23.2, 22.7 ppm (CH$_3$); MS (70 eV): *m*/*z* (%): 386 (88) [$M-$H]$^+$; elemental analysis calcd (%) for C$_{21}$H$_{23}$NO$_2$S$_2$: C 65.42, H 6.01, N 3.63, S 16.63; found: C 65.85, H 5.94, N 3.38, S 16.12.

2,3-Di(isopropylmercapto)benzoyl amine (6): A solution of **5** (1.40 g, 3.63 mmol) in ethanol (40 mL) was treated with hydrazine monohydrate (309 mg, 6.17 mmol). The reaction mixture was heated under reflux for

2 h. Then an excess of hydrochloric acid was added. The reaction mixture was filtered and the remaining solids were washed with water. The majority of the ethanol was removed under vacuum and sodium hydroxide was added to the remaining solution until a basic pH was reached. The mixture was extracted three times with diethyl ether (30 mL each) and the combined ether phases were dried over Na_2SO_4. After removal of the solvent under vacuum compound **6** was obtained as a yellow oil (640 mg, 2.51 mmol, 69 %). ^{1}H NMR (400 MHz, [D$_7$]DMF): $\delta=7.23$ (t, 1H; Ar-H), 7.13 (d, 1H; Ar-H), 7.12 (d, 1H; Ar-H), 4.03 (s, 2H; CH_2), 3.47 (sept, 1H; $\mathrm{C}\mathit{H}(\mathrm{CH}_3)_2$), 3.46 (sept, 1H; $\mathrm{C}\mathit{H}(\mathrm{CH}_3)_2$), 1.96 (br s, 2H; NH_2), 1.36 (d, 6H; CH_3), 1.20 ppm (d, 6H; CH_3); ^{13}C NMR (100 MHz, [D$_7$]DMF): $\delta=148.3$, 145.4, 130.9, 129.1, 125.3, 124.7 (Ar-C), 45.9 (CH_2), 39.0, 35.8 (CH), 23.1, 22.7 ppm (CH_3); elemental analysis calcd (%) for $C_{13}H_{21}NS_2$: C 61.13, H 8.29, N 5.48, S 25.10; found: C 60.48, H 8.03, N 4.83, S 25.89.

Ligand precursor 7: Freshly prepared 2,3-di(isopropylmercapto)benzoic acid (317 mg, 1.17 mmol) was converted into the acid chloride **1** by using oxalyl chloride in benzene. After removal of the solvent the formed **1** (a 98 % conversion was assumed) was dissolved in THF (20 mL). This solution was added to a solution made up from **4** (300 mg, 1.17 mmol) and NEt_3 (178 mg, 1.76 mmol) dissolved in THF (40 mL). The reaction mixture was stirred for 12 h at ambient temperature. It was then filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane 1:1, v/v) to give **7** as a white solid (590 mg, 1.16 mmol, 99 %). ^{1}H NMR (400 MHz, [D$_7$]DMF): $\delta=7.41$ (dd, ^3J(H,H) = 6.7 Hz, ^4J(H,H) = 2.4 Hz, 1H; Ar-H); 7.38 (dd, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.3 Hz, 1H; Ar-H); 7.28 (t, ^3J(H,H) = 6.7 Hz, 1H; Ar-H); 7.27 (d, ^3J(H,H) = 6.7 Hz, 1H; Ar-H); 7.26 (t, ^3J(H,H) = 7.8 Hz, 1H; Ar-H); 7.19 (dd, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.3 Hz, 1H; Ar-H); 7.13 (t, ^3J(H,H) = 6.2 Hz, 1H; N-H); 4.89 (d, ^3J(H,H) = 6.2 Hz, 2H; CH_2); 3.49, 3.48, 3.46, 3.32 (4 × sept, ^3J(H,H) = 6.7 Hz, 1H; $\mathrm{C}\mathit{H}(\mathrm{CH}_3)_2$); 1.38, 1.36, 1.24, 1.09 ppm (4 × d, ^3J(H,H) = 6.7 Hz, 6H; CH_3); ^{13}C NMR (100 MHz, [D$_7$]DMF): $\delta=168.3$ C(O)NH), 145.6, 145.5, 143.7, 142.8, 131.5, 129.2, 129.1, 128.8, 127.9, 126.1, 125.9, 125.5 (Ar-C), 43.5 (CH_2), 40.6, 39.3, 36.1, 35.9 (CH), 23.2, 22.8, 22.7, 22.7 ppm (CH_3); elemental analysis calcd (%) for $C_{26}H_{37}NOS_4$: C 61.49, H 7.34, N 2.76, S 25.26; found: C 62.12, H 7.44, N 2.52, S 25.88.

Ligand H$_4$-8: Dry, freshly distilled THF (60 mL) was added to a mixture of compound **7** (500 mg, 0.98 mmol), sodium (227 mg, 9.87 mmol), and naphthalene (631 mg, 4.85 mmol). The reaction mixture was stirred for 12 h at ambient temperature. Subsequently methanol (10 mL) was added to remove unreacted sodium. The solvents were then removed under vacuum. The solid residue was dissolved in degassed water and the resulting solution was washed three times with degassed diethyl ether (20 mL each). The aqueous solution was filtered and HCl (37 %) was added dropwise until a white precipitate formed. This precipitate was isolated by filtration and washed with water and diethyl ether. The solid residue was dried under vacuum to give ligand H$_4$-**8** as a beige powder (310 mg, 0.91 mmol, 93 %). ^{1}H NMR (400 MHz, [D$_7$]DMF): $\delta=9.07$ (t, ^3J(H,H) = 5.7 Hz, 1H; N-H), 7.62 (dd, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 1.4 Hz, 1H; Ar-H), 7.50 (dd, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.3 Hz, 1H; Ar-H), 7.49 (dd, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 1.4 Hz, 1H; Ar-H), 7.28 (dd, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.3 Hz, 1H; Ar-H), 7.13 (t, ^3J(H,H) = 7.9 Hz, 1H; Ar-H), 7.13 (t, ^3J(H,H) = 7.9 Hz, 1H; Ar-H), 5.49 (br s, 4H; S-H), 4.67 ppm (d, ^3J(H,H) = 5.7 Hz, 2H; CH_2); ^{13}C NMR (100 MHz, [D$_7$]DMF): $\delta=169.8$ (C(O)N), 139.4, 135.2, 134.2, 132.1, 129.3, 129.0, 126.9, 126.2, 126.2, 125.5 (Ar-C, only 10 signals were observed for the 12 aromatic carbon atoms), 43.4 ppm (CH_2); elemental analysis calcd (%) for $C_{14}H_{13}NOS_4$: C 49.53, H 3.86, N 4.13, S 37.77; found: C 49.34, H 3.90, N 3.96, S 36.88.

Preparation of (Ph$_4$As)$_4$[Ti$_2$(3)$_3$] ((Ph$_4$As)$_4$[9]): A sample of [Ti(OPr)$_4$] (19.0 mg, 0.067 mmol) was added to a solution of H$_4$-**3** (50 mg, 0.10 mmol) and Na_2CO_3 (7.0 mg, 0.067 mmol) in degassed methanol (20 mL). The solution was stirred under argon at ambient temperature for 12 h and filtered. Addition of Ph_4AsCl (58 mg, 0.134 mmol) to the filtrate yielded a dark red precipitate, which was isolated by filtration, washed with methanol (2 × 10 mL), and dried under vacuum. Yield: 92 mg (0.028 mmol, 83 %; 66 % after recrystallization); ^{1}H NMR (400 MHz, [D$_7$]DMF): $\delta=11.38$ (s, 6H; N-H), 8.25 (d, ^3J(H,H) = 8.2 Hz, 6H; naphthalene-H), 7.95 (m, 16H; Ph-H), 7.86 (m, 32H; Ph-H), 7.84 (m, 32H; Ph-H), 7.66 (d, ^3J(H,H) = 8.2 Hz, 6H; naphthalene-H), 7.59 (dd, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.3 Hz, 6H; Ar-H), 7.21 (dd, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.3 Hz, 6H; Ar-H), 7.13 (t, ^3J(H,H) = 8.2 Hz, 6H; naphthalene-H), 6.83 ppm (t, ^3J(H,H) = 7.7 Hz, 6H; Ar-H); ^{13}C NMR (100 MHz, [D$_7$]DMF): $\delta=167.8$ (C(O)NH), 156.4, 151.6 (C-S), 135.1, 134.2, 131.7, 122.1 (Ph-C), 133.6, 129.4, 125.2, 121.9 (Ar-C), 135.5, 129.5, 126.2, 121.3, 121.1 ppm (naphthalene-C); MS (ESI, negative ions): *m*/*z*: 784.3 $[\mathrm{Ti_2}(\mathbf{3})_3+2\mathrm{H}]^{2-}$, 523.1 $[\mathrm{Ti_2}(\mathbf{3})_3+\mathrm{H}]^{3-}$, 392.1 $[\mathrm{Ti_2}(\mathbf{3})_3]^{4-}$.

Preparation of (Et$_4$N)$_4$[Ti$_2$(3)$_3$] ((Et$_4$N)$_4$[10]): The compound was prepared as described for (Ph$_4$As)$_4$[Ti$_2$(**3**)$_3$] with the exception that Et_4NBr (28 mg, 0.134 mmol) was added for precipitation. Yield: 66 mg (0.026 mmol, 78 %; 60 % after recrystallization); ^{1}H NMR (400 MHz, [D$_7$]DMF): $\delta=11.25$ (s, 6H; N-H), 8.29 (d, ^3J(H,H) = 7.8 Hz, 6H; naphthalene-H), 7.77 (d, ^3J(H,H) = 7.8 Hz, 6H; naphthalene-H), 7.51 (dd, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.3 Hz, 6H; Ar-H), 7.25 (t, ^3J(H,H) = 7.8 Hz, 6H; naphthalene-H), 7.20 (dd, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.3 Hz, 6H; Ar-H), 6.84 (t, ^3J(H,H) = 7.7 Hz, 6H; Ar-H), 3.19 (q, $^3J=7.4$ Hz, 32H; N-CH_2), 1.18 ppm (t, ^3J(H,H) = 7.4 Hz, 48H; CH_3); ^{13}C NMR (100 MHz, [D$_7$]DMF): $\delta=168.3$ (C(O)NH), 156.5, 151.2 (C-S), 133.6, 129.2, 124.6, 121.8 (Ar-C), 135.7, 129.5, 126.3, 121.4, 121.2 (naphthalene-C), 52.5 (CH_2), 7.5 ppm (CH_3); MS (ESI, negative ions): *m*/*z*: 914.4 $[\mathrm{Ti_2}(\mathbf{3})_3+2\mathrm{Et_4N}]^{2-}$, 784.3 $[\mathrm{Ti_2}(\mathbf{3})_3+2\mathrm{H}]^{2-}$, 566.1 $[\mathrm{Ti_2}(\mathbf{3})_3+\mathrm{Et_4N}]^{3-}$, 523.1 $[\mathrm{Ti_2}(\mathbf{3})_3+\mathrm{H}]^{3-}$, 392.1 $[\mathrm{Ti_2}(\mathbf{3})_3]^{4-}$.

Preparation of (Bu$_4$N)$_4$[Ti$_2$(3)$_3$] ((Bu$_4$N)$_4$[11]): The compound was prepared as described for (Ph$_4$As)$_4$[Ti$_2$(**3**)$_3$] with the exception that Bu_4NCl (40 mg, 0.134 mmol) was added for precipitation. Yield: 53 mg (0.021 mmol, 63 %; 42 % after recrystallization); ^{1}H NMR (400 MHz, [D$_7$]DMF; signals given for both isomeric species: ◆ marks signals of the helical complex anion): $\delta=11.40$ (s, 6H; N-H, ◆), 10.94 (s, 2H; N-H), 10.29 (s, 4H; N-H), 8.95 (d, ^3J(H,H) = 8.4 Hz, 2H; naphthalene-H), 8.29 (d, ^3J(H,H) = 8.4 Hz, 6H; naphthalene-H, ◆), 7.70 (d, ^3J(H,H) = 7.5 Hz, 6H; naphthalene-H, ◆), 7.62 (dd, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.5 Hz, 6H; Ar-H, ◆), 7.53 (d, ^3J(H,H) = 7.4 Hz, 2H; Ar-H), 7.52 (d, ^3J(H,H) = 7.4 Hz, 2H; naphthalene-H), 7.52 (d, ^3J(H,H) = 7.4 Hz, 4H; Ar-H), 7.44 (d, ^3J(H,H) = 8.4 Hz, 4H; naphthalene-H), 7.31 (dd, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.3 Hz, 4H; Ar-H), 7.25 (t, ^3J(H,H) = 8.4 Hz, 2H; naphthalene-H), 7.23 (dd, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.5 Hz, 6H; Ar-H, ◆), 7.19 (d, ^3J(H,H) = 7.5 Hz, 2H; Ar-H), 7.17 (t, ^3J(H,H) = 7.3 Hz, 6H; naphthalene-H, ◆), 7.06 (br s, 4H; naphthalene-H, at ambient temperature; d, ^3J(H,H) = 7.3 Hz, at 310 K), 6.97 (t, ^3J(H,H) = 7.7 Hz, 2H; Ar-H), 6.89 (t, ^3J(H,H) = 7.7 Hz, 4H; Ar-H), 6.89 (t, ^3J(H,H) = 7.7 Hz, 4H; naphthalene-H), 6.87 (t, ^3J(H,H) = 7.7 Hz, 6H; Ar-H, ◆), 3.29 (m, 32H; N-CH_2), 1.67 (m, 32H; N-$\mathrm{CH_2}$-$\mathrm{C}\mathit{H}_2$-$\mathrm{CH_2}$), 1.34 (sext, ^3J(H,H) = 7.4 Hz, 32H; $\mathrm{CH_2}$-$\mathrm{C}\mathit{H}_2$-$\mathrm{CH_3}$), 0.91 ppm (t, ^3J(H,H) = 7.4 Hz, 48H; CH_3); ^{13}C NMR (100 MHz, [D$_7$]DMF): $\delta=167.8$ (C(O)NH, ◆), 167.1, 166.9 (C(O)NH), 156.4 (C-S, ◆), 155.2, 154.3, 152.5, 152.2 (C-S), 151.6 (C-S, ◆), 136.7 (Ar-C) 133.7 (Ar-C, ◆), 133.4 (Ar-C), 129.6 (Ar-C, ◆), 129.6, 128.6 (Ar-C), 125.2 (Ar-C, ◆), 124.7, 123.8, 123.1, 122.7 (Ar-C), 121.9 (Ar-C, ◆), 135.6 (naphthalene-C, ◆), 134.0, 133.9 (naphthalene-C), 129.6 (naphthalene-C, ◆), 129.0 (naphthalene-C), 126.3 (naphthalene-C, ◆), 125.2, 125.1, 124.7, 122.3 (naphthalene-C), 121.3 (naphthalene-C, ◆), 121.2 (naphthalene-C, ◆), 120.2, 119.2, 116.5 (naphthalene-C), 58.8 (N-CH_2), 24.2 ($\mathrm{CH_2}$-$\mathit{C}\mathrm{H_2}$-$\mathrm{CH_2}$), 20.1 ($\mathrm{CH_2}$-$\mathit{C}\mathrm{H_2}$-$\mathrm{CH_3}$), 13.8 ppm (CH_3); MS (ESI, negative ions): *m*/*z*: 522.3 $[\mathrm{Ti_2}(\mathbf{3})_3+\mathrm{H}]^{3-}$, 603.1 $[\mathrm{Ti_2}(\mathbf{3})_3+4\,\mathrm{Bu_4N}]^{3-}$.

Preparation of (Ph$_4$As)$_4$[Ti$_2$(8)$_3$] ((Ph$_4$As)$_4$[12]): A sample of [Ti(OPr)$_4$] (27.9 mg, 0.098 mmol) was added to a solution of H$_4$-**8** (50 mg, 0.147 mmol) and Na_2CO_3 (10.4 mg, 0.098 mmol) in degassed methanol (20 mL). The solution was stirred under argon at ambient temperature for 12 h and then filtered. Addition of Ph_4AsCl (86 mg, 0.197 mmol) to the filtrate yielded a dark red precipitate, which was isolated by filtration, washed with methanol (2 × 10 mL), and dried under vacuum. Yield: 102 mg (0.036 mmol, 73 %); ^{1}H NMR (400 MHz, [D$_7$]DMF, 300 K): $\delta=10.17$ (t, 3H; N-H), 10.10 (t, 1H; N-H), 9.81 (m, 2H; N-H), 7.93 (m, 16H; Ph-H), 7.83 (m, 32H; Ph-H), 7.78 (m, 32; Ph-H), 7.63, 7.54, 6.92, 6.91, 6.69, 6.68, 6.64, 6.58, 6.45, 6.41, 6.29, 6.28 (Ar-H), 4.67, 3.90 ppm (CH_2); ^{13}C NMR (100 MHz, [D$_7$]DMF, 300 K): $\delta=167.8$, 167.4 (CO), 156.6, 156.5, 154.3, 154.3, 154.2, 154.0, 152.0, 151.5 (C-S), 135.2, 134.0, 131.8, 121.8 (Ph-C), 135.1, 134.9, 132.0, 131.9, 128.9, 128.7, 126.9, 126.3, 126.1, 125.5, 124.7, 124.1, 120.9, 120.7, 120.7, 120.6 (Ar-C), 44.8, 44.6 ppm (CH_2); three sets of resonances were expected: one for the ligand strands in the anion with a parallel ligand orientation and two more for the anion with the antiparallel orientation; however, not all signals could be resolved with the exception of the N-H resonances in the ^1H NMR spectrum; MS (ESI, negative ions): m/z: 367.5 $[Ti_2(\mathbf{8})_3+H]^{3-}$, 380.1 $[Ti_2(\mathbf{2})_3+K]^{3-}$.

X-ray crystallography: X-ray diffraction data were collected on a Bruker AXS APEX diffractometer ($(Ph_4As)_4[\mathbf{9}]\cdot 2Et_2O$ and $(Et_4N)_4[\mathbf{10}]\cdot 2DMF\cdot H_2O$) or on an Enraf-Nonius Kappa CCD ($(Bu_4N)_4[\mathbf{11}]$) both equipped with a rotating anode and with $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). Empirical absorption corrections using the program SADABS[26] were applied to the raw data for $(AsPh_4)_2[\mathbf{9}]\cdot 2Et_2O$ ($0.28 \leq T \leq 0.83$) and $(Et_4N)_4[\mathbf{10}]\cdot 2DMF\cdot H_2O$ ($0.34 \leq T \leq 0.81$). Program SORTAV[27] was used for absorption corrections to the raw data of $(NBu_4)_4[\mathbf{11}]$ ($0.77 \leq T \leq 0.55$). Structure solutions were found with SHELXS[28] in all cases and the refinement was carried out with SHELXL[29] using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions and were refined as riding atoms.

Crystal data for $(Ph_4As)_4[Ti_2(\mathbf{3})_3]\cdot 2Et_2O$: $C_{176}H_{142}N_6As_4O_8S_{12}Ti_2$; $M_r = 3249.16$; crystal size $0.43 \times 0.17 \times 0.05$ mm^3; monoclinic; space group $P2_1/n$; $a = 19.4830(8)$, $b = 13.8938(6)$, $c = 28.3429(11)$ Å; $\beta = 104.625(2)°$; $V = 7423.6(5)$ Å^3; $Z = 2$; $2\theta_{max} = 130.0°$; $\lambda = 1.54178$ Å; $\mu(Cu) = 3.987$ mm^{-1}; $T = 153(2)$ K; 40787 measured reflections; 12508 independent reflections used in refinement against $|F^2|$; $R = 0.0589$, $wR = 0.1593$ (for 7902 reflections $I \geq 2\sigma(I)$).

Crystal data for $(Et_4N)_3[Ti_2(\mathbf{3})_3]\cdot 2DMF\cdot H_2O$: $C_{110}H_{138}N_{12}O_9S_{12}Ti_2$; $M_r = 2552.86$; crystal size $0.37 \times 0.10 \times 0.06$ mm^3; monoclinic; space group $P2_1/c$; $a = 18.4943(9)$, $b = 37.426(2)$, $c = 16.5461(9)$ Å; $\beta = 93.488(3)°$; $V = 11431.6(10)$ Å^3; $Z = 4$; $2\theta_{max} = 135.0°$; $\lambda = 1.54178$ Å; $\mu(Cu) = 3.717$ mm^{-1}; $T = 153(2)$ K; 65493 measured reflections; 20313 independent reflections used in refinement against $|F^2|$; $R = 0.1136$, $wR = 0.2964$ (for 6711 reflections $I \geq 2\sigma(I)$).

Crystal data for $(Bu_4N)_4[Ti_2(\mathbf{3})_3]$: $C_{136}H_{186}N_{10}O_6S_{12}Ti_2$; $M_r = 2537.47$; crystal size $0.25 \times 0.10 \times 0.10$ mm^3; monoclinic; space group $C2/c$; $a = 55.5199(13)$, $b = 17.1842(5)$, $c = 33.4814(9)$ Å; $\beta = 94.500(1)°$; $V = 31845.0(15)$ Å^3; $Z = 8$; $\mu(Cu) = 26.97$ cm^{-1}; $\lambda = 1.54178$ Å; $T = 223(2)$ K; 119766 measured reflections; 22460 independent reflections used in refinement against $|F^2|$; $R = 0.0964$, $wR = 0.2591$ (for 11307 reflections $I \geq 2\sigma(I)$).

CCDC-674837 ($(AsPh_4)_2[\mathbf{9}]\cdot 2Et_2O$), CCDC-674838 ($(Et_4N)_4[\mathbf{10}])\cdot 2DMF\cdot H_2O$), and CCDC-712005 ($(Bu_4N)_4[\mathbf{11}]$) 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.

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