Anion Recognition

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Highly Efficient Extraction of Sulfate Ions with a Tripodal Hexaurea Receptor**

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The design of artificial receptors for sulfate ions is of great interest because of the importance of sulfate ions in environmental and biological systems.[1] One of the applications of sulfate ion receptors is extraction of the sulfate ion from nitrate-rich mixtures in the remediation of nuclear waste.[2] Based on liquid–liquid anion exchange technology, extraction of sulfate ions from an aqueous to an organic phase was realized by using macrocyclic receptors.[2b] In particular, the distribution ratio ($D_{sulfate} = [SO_4^{2-})]_{org}/[SO_4^{2-})]_{aq}$) can reach technologically useful values (>1) when a fluorinated calixpyrrol is used.[2c] However, high concentrations (about 1000 times SO_4^{2-}) of the receptor were needed in this case to ensure applicable extraction. Hence, the extraction efficiency has yet to be improved for sulfate ion extractants. This aim is quite challenging because of the extremely large hydration energy of the sulfate ion ($\Delta G_h = -1080\ kJ\,mol^{-1}$ for SO_4^{2-} compared to $-300\ kJ\,mol^{-1}$ for NO_3^-)[3] according to the Hofmeister series,[4] as well as the high nitrate/sulfate ratios present in the crude waste. To overcome the Hofmeister bias, which disfavors the separation of the extremely hydrophilic sulfate ion from water, the receptor must have both excellent affinity and selectivity for sulfate ions.

In recent years, some receptors for sulfate ions have been synthesized by employing different binding groups (mostly NH moieties), such as protonated Schiff base macrocycles,[5] diindolylureas,[6] and an M_4L_6 cage containing a bipyridine-functionalized monourea;[7] these receptors bind the anion in the 1:1, 3:1 and 6:1 (host/guest) mode, respectively. The tren-based tripodal trisurea backbone (L^1; tren = tris(2-aminoethyl)amine) has also been found to encapsulate the sulfate ion in a 2:1 (host/guest) ratio.[8] Although saturated coordination (12 hydrogen bonds) for sulfate and phosphate ions has been achieved by these receptors, the complementarity for the ions is not optimal in most cases. Calculations have demonstrated that the optimal saturated coordination mode for sulfate ions is binding in a tetrahedral cavity with 12 hydrogen bonds along the edges.[9] In this regard, the ideal sulfate ion receptor would possess a complementary tetrahedral cavity surrounded by 12 optimally arranged binding sites.

The chelate effect may also play an important role in the host–guest binding affinity because of the favorable contributions from both entropy and enthalpy. As a typical example of the chelate effect, the Co^{2+} complex of the bidentate ligand 1,2-diaminoethane is 10^8 times more stable than that of the unidentate ligand ammonia.[10] Moreover, the hexadentate ligand ethylenediaminetetraacetic acid (EDTA) displays extremely high binding affinities toward most metal ions (for example, $10^{14.3}\ M^{-1}$ for Fe^{2+} and $10^{16.3}\ M^{-1}$ for Co^{2+}).[11] Given the similarities between anion coordination and classical transition-metal coordination chemistry,[12] increasing the number of binding sites to achieve high chelate effects should be an effective way to improve the extraction efficiency of sulfate ion extractants.

We have devoted our efforts to the synthesis of selective anion receptors based on the urea functionality.[8a,13] In recent work, we designed a trisurea receptor (L^2, Scheme 1a) for sulfate and phosphate ions by mimicking the terpyridine scaffold, which displays a fully complementary conformation with the tetrahedral anions and achieves saturated coordination with PO_4^{3-} ions in a 2:1 (host/guest) binding mode.[13a] Compared to the 2:1 sulfate capsule of the tripodal receptor L^1, in which one of the ligands shows a complementary conformation with the three axial edges but the other ligand contacts with the vertices of the bottom triangular face (Scheme 1b) of the sulfate ion, both molecules of L^2 adopt favorable conformations in the 2:1 phosphate ion complex. The results indicate that the *ortho*-substituted phenyl bridge may serve as a suitable "corner" (or vertex) in constructing tetrahedral cages for sulfate and phosphate ions. Based on the sulfate ion binding properties of L^1 and L^2, it is reasonable to believe that a combination of the properties, that is, incorporation of both the excellent complementarity and chelate effect in one molecule, may lead to an excellent extraction efficiency for sulfate ions.

With this approach in mind, we extended each of the three monourea arms of L^1 to an *ortho*-phenyl bridged bisurea (Scheme 1) to produce a hexaurea ligand (L^3). The receptor L^3 was readily synthesized by reaction of *p*-nitro-phenyl-

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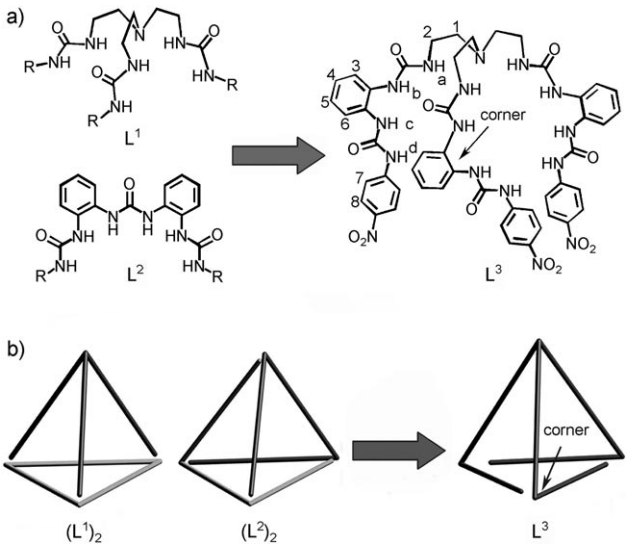


Scheme 1. Design strategy for the tripodal hexaurea receptor L^3. a) Structures of L^1 (R = 3-pyridyl), L^2 (R = *p*-nitrophenyl), and L^3; b) schematic illustration of the construction of the tetrahedral cage.

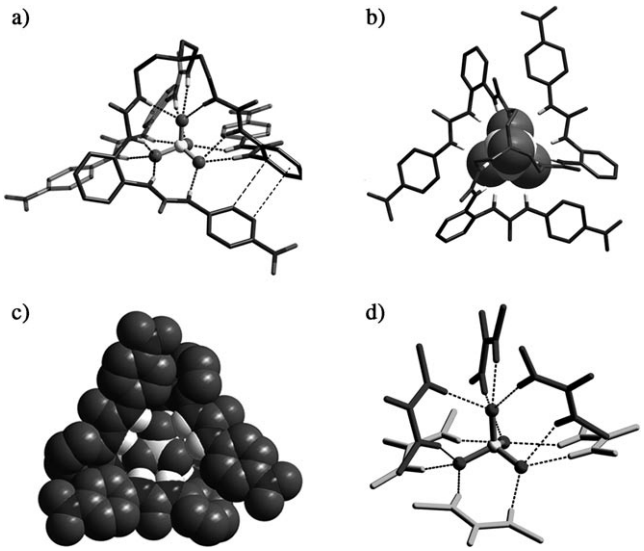


Figure 1. Crystal structure of the sulfate complex **1**: a) side view showing the hydrogen bonds and CH···π interactions (only one of the three pairs is shown); b, c) top and bottom views showing the tight binding of the sulfate ion (non-acidic hydrogen atoms, solvents, and countercations omitted for clarity); d) arrangement of the 6 urea groups that donate 12 hydrogen bonds to the sulfate ion.

isocyanate with tris(2-aminophenyl)urea, which was reduced from tris(2-nitrophenyl)urea (L^{1a}).[14] X-ray diffraction analysis[15] of the free receptor L^3 indicates that the three outer urea arms are tilted up from the phenyl bridges in a folding-umbrella fashion, and the urea groups are involved in either intra- or intermolecular urea···urea self-association to lead to a hydrogen-bonded 1D chain. There are also additional intra- and intermolecular π–π stacking interactions between the terminal *p*-nitrophenyl groups (see the Supporting Information for details).

Single crystals of the sulfate complex of L^3, $(TBA)_2[L^3SO_4]\cdot DMSO$ (**1**)[15] were obtained by slow evaporation of a 1:1 (v/v) water/DMSO solution of the receptor in the presence of excessive $(TBA)_2SO_4$ (TBA = tetrabutylammonium). Notably, when other anions such as $(TBA)H_2PO_4$, (TBA)AcO, and (TBA)Cl were used, only the free receptor was crystallized, which may reveal a specific strong binding with sulfate in aqueous environments. In contrast to the divergent conformation of the free receptor, in complex **1** (Figure 1), each of the three terminal arms is folded along an edge of the bottom triangular face (while the three inner urea groups occupy the axial edges), thus completing a tetrahedral cage to encapsulate the sulfate ion. The complementarity achieved by complex **1** fulfils our expectation that all six urea groups are involved in binding with the anion; each urea group chelates an edge of the tetrahedron to form a total of twelve hydrogen bonds (N–O distances ranging from 2.903 to 3.157 Å, average distance 2.992 Å; N-H-O angles ranging from 142.6° to 172.6°, average angle 160.5°; Table S3 in the Supporting Information) between the receptor and the sulfate ion. In addition, there are three pairs of T-shaped CH···π interactions between the terminal *p*-nitrophenyl and adjacent 1,2-substituted phenyl groups, both of which are located near the vertices of the bottom triangle (C–π distances ranging from 3.51 to 3.61 Å; Figure 1a and Figure S2 in the Supporting Information).[16] To the best of our knowledge, L^3 is the only receptor reported to date that shows saturated coordination (12 hydrogen bonds) of a sulfate ion by a single organic molecule.

The interactions between L^3 and the sulfate ion (added as the TBA salt) in solution were studied by ^{1}H NMR experiments. Two slow exchange processes were observed during the titration of two equivalents of sulfate ions in a $[D_6]$DMSO/0.5% water solution. This observation is rationalized by a two-step binding mechanism involving the change of the binding mode from 1:1 to 1:2 (host/guest; Figure 2). In the first step, when 0.5 equivalents of sulfate ions were added, all the NH signals experienced considerable downfield shifts,

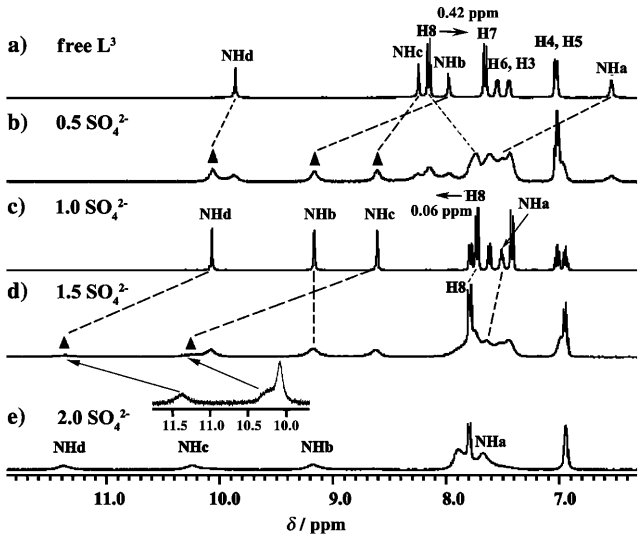


Figure 2. ^{1}H NMR ($[D_6]$DMSO/0.5% D_2O, 400 MHz) spectra of L^3 (5 mM) in the presence of SO_4^{2-} ions. The symbol ▲ denotes the new NH signals, overlapped peaks are not marked.

thus indicating the cooperative binding of the sulfate ion by all the NH groups, most likely in a similar fashion to the solid-state structure of complex **1**. Nevertheless, the shifts ($\Delta\delta$, ppm) of the "inner" urea groups NHa ($\Delta\delta = 0.98$) and NHb ($\Delta\delta = 1.17$) are remarkably larger than the "outer" NHc ($\Delta\delta = 0.36$) and NHd ($\Delta\delta = 0.19$), thus implying that the bound sulfate ion is located in the "inner" position of the tetrahedral cavity and is closer to NHa and NHb than to NHc and NHd. The first step was finished after one equivalent of sulfate ions was added, at which point the receptor formed the 1:1 complex with the sulfate ion, and the signals of the free receptor disappeared completely. In the second step, a new set of signals appeared as more sulfate ions were added; this result may be attributed to the formation of the 1:2 (host/guest) species. In contrast to the first step, the downfield shifts ($\Delta\delta$, ppm) of the outer NHc ($\Delta\delta = 1.63$) and NHd ($\Delta\delta = 1.32$) groups were greater than those of the inner groups, which showed only slight (NHa, $\Delta\delta < 0.2$) or no changes (NHb) in this step, thus indicating that the outer arms with NHc and NHd were opened to bind the second sulfate ion. Although the structure of the 1:2 complex is unclear, the NMR signals are broadened rather than sharp as in the 1:1 complex, and may be average signals that arise from rapid equilibration of multiple binding modes (Figure 2). The changes were completed after addition of two equivalents of sulfate ions. Additionally, the upfield shift ($\Delta\delta = 0.42$ ppm) of the hydrogen atom H8 on the terminal aryl ring (see Scheme 1 for atom numbering) in the first step followed by a slight downfield shift ($\Delta\delta = 0.06$ ppm) in the second step also implies that the change of conformation and binding mode occurred in the two-step binding process.[13a]

Interestingly, in the presence of 10% or 25% D_2O (more water will cause precipitation), the 1:1 binding mode became the only stable form, as supported by the fact that addition of one equivalent of sulfate ions resulted in saturation and no further changes were observed upon further addition of the anion (Figure 3). Since the NH signals did not appear in the presence of D_2O, the binding affinity was evaluated by the upfield shift of H8. As mentioned above, in the 1:1 complex, the proximity of the terminal *p*-nitrophenyl and the bridging 1,2-substituted phenyl groups can lead to significant shielding (and an upfield shift) of H8. Thus the upfield shift of this proton, which can be monitored in NMR titrations, may serve as evidence for the structure of **1**. Such a shielding effect has also been reported in foldamer formation[17] and in our previous work on the 2:1 phosphate complex of L^2.[13a] In general, a dramatic decrease of the binding affinity is expected as the percentage of water in the solution increases because of the highly competitive effect of water. Biological proteins, such as the sulfate-binding protein (SBP), overcome this problem by fully encapsulating the anion in a pocket with a hydrophobic surface, which can avoid the strong competition with water.[18] Encouragingly, the binding behavior of L^3 displays a similar water-tolerant property as almost identical upfield shifts of H8 were induced by one equivalent of sulfate ions ($\Delta\delta = 0.39$–0.42 ppm), regardless of the amount of water in the titration system (from 0.5% to 25%). In accordance with the SBP, the main competitive effect from water may have been excluded by the complete encapsulation of the anion in the tetrahedral cavity that is protected by hydrophobic aromatic phenyl rings (Figure 1c).

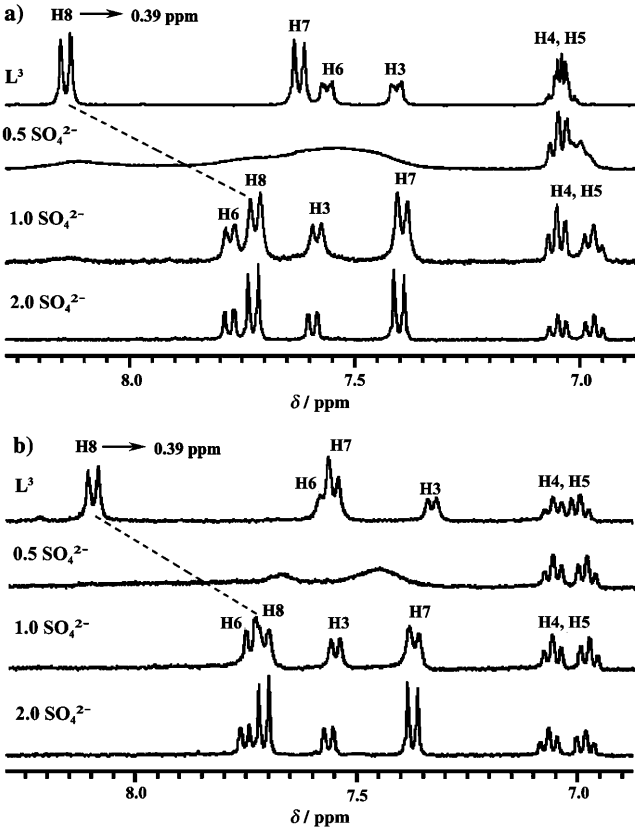


Figure 3. ^{1}H NMR (400 MHz) spectra of L^3 (1 mM) in the presence of various equivalents of SO_4^{2-} ions (added as TBA salt) in a) [D_6]DMSO/10% D_2O and b) [D_6]DMSO/25% D_2O solution.

Competitive experiments with other anions were carried out in the presence of 25% D_2O. The results demonstrated that L^3 selectively binds sulfate ions over equal amounts of various competitive anions, and the selectivity follows the sequence $SO_4^{2-} > H_2PO_4^- \gg$ other anions (Figure S3 in the Supporting Information). Although the association constant for sulfate ions could not be accurately determined by UV/Vis titration because of the irregular (in DMSO) or too weak (in DMSO/10% or 25% H_2O) colorimetric changes induced by the anion, the association constant can be estimated from the ^{1}H NMR titration data to be larger than $10^4\,M^{-1}$, even in the presence of 25% D_2O, because one equivalent of sulfate ions resulted in a completely saturated spectrum.[19]

As L^3 has a water-tolerant nature and selectivity for sulfate ions, we then studied the extraction behavior of this ligand by ^{1}H NMR spectroscopy. A solution containing $NaNO_3$ (blank, Figure 4a) or $Na_2SO_4/NaNO_3$ (1:10; Figure 4b) in deionized water (0.5 mL) was layered onto a solution of L^3 and (TBA)Cl in $CDCl_3$ (0.5 mL) in an NMR tube ((TBA)Cl was used to aid the dissolution of L^3 in $CDCl_3$ and exchange with sulfate ions). The two layers were thoroughly mixed for 10 seconds and allowed to settle for 10 seconds, during which time the two layers separated and the organic phase was immediately analyzed. The resulting aqueous layers in the two experiments were shown by UV/Vis

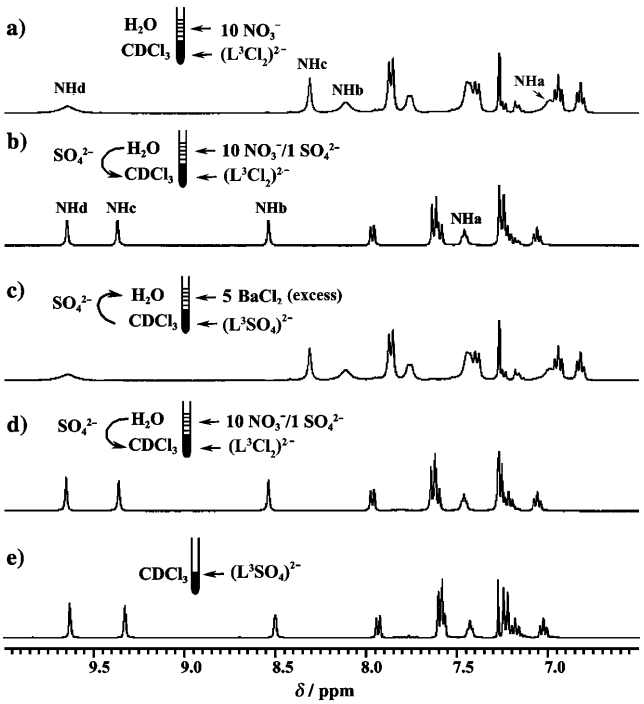


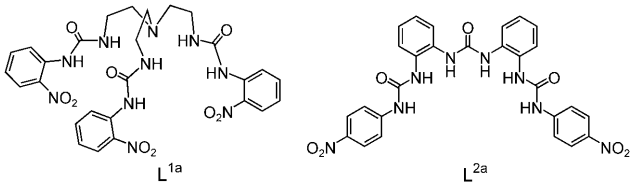
Figure 4. ^{1}H NMR spectra (400 MHz, $CDCl_3$, L^3 10 mM) of a) blank, b) sulfate extraction, c, d) recycling, and e) comparison experiments, indicating the nearly quantitative and recyclable extraction of sulfate from water to $CDCl_3$ phase (numbers represent the number of ion equivalents).

spectroscopy to contain only a trace of L^3 (< 30 μM; Figure S4 in the Supporting Information). Comparison experiments (in organic solution only and in the absence of nitrate ions) were also conducted by directly adding aliquots of sulfate ions (as the TBA salt) to a $CDCl_3$ solution of L^3/(TBA)Cl. The NMR signals corresponding to the chloride- and sulfate-binding receptor appeared independently as a result of slow proton exchange, and the original signals disappeared completely when the amount of sulfate ions reached one equivalent. No further changes were observed as more sulfate ions were added, which is consistent with a 1:1 binding mode (Figure S5 in the Supporting Information). The spectrum of the extraction experiment in the presence of excess nitrate ions agreed well with that induced by one equivalent of sulfate ions in the comparison experiments, thus indicating that nearly all the sulfate ions (one equivalent) in the aqueous layer were extracted into the $CDCl_3$ phase.

The sulfate-binding receptor in $CDCl_3$ can be readily returned to the chloride-binding form by extracting the sulfate ions with an aqueous solution of $BaCl_2$ (0.5 mL, 50 mM; Figure 4c). In the back-extraction process with 1–5 equivalents of $BaCl_2$, increasing amounts of sulfate ions were extracted as a white suspension of $BaSO_4$ in H_2O. The spectrum of the resulting organic layer was analyzed immediately after each extraction. As a result of slow proton exchange, a new set of signals corresponding to the regenerated receptor appeared and gradually increased, and the concentrations of the chloride-binding and sulfate-binding receptor were determined based on the proton integral ratios (Figure S6 in the Supporting Information). From these data, together with the solubility product constant K_{sp} of $BaSO_4$ and the concentrations of Ba^{2+} thus deduced, the apparent sulfate binding constant K_{app} ($K(LSO_4)/K(LCl_2)$) under the extraction conditions was calculated as 1.2×10^3 M (see the Supporting Information).[7] This process also enabled a direct evaluation of the extraction efficiency by the gravimetric method which indicated an extraction yield higher than 95% (Table S6 in the Supporting Information).

Furthermore, the repeatability of the sulfate extraction was examined by replacing the aqueous suspension of $BaSO_4$ with a fresh aqueous solution of 10 mM Na_2SO_4/100 mM $NaNO_3$. As shown in Figure 4d, the extraction of sulfate ions is repeatable, thus implying that L^3 can be recycled when used as a sulfate ion extractant. Control experiments performed in the presence of an excess of nitrate ions (from 10 to 100 equivalents) demonstrated that the sulfate ion extraction ability of L^3 was not noticeably influenced by the presence of a large excess of nitrate ions (Figure S7 in the Supporting Information).

For comparison, parallel extraction experiments with the trisurea ligands L^{1a} or L^{2a} (Scheme 2) were also carried out under similar conditions. In contrast to the high efficiency of



Scheme 2. Structures of L^{1a} and L^{2a}.

L^3, the sulfate ion extraction abilities of the two receptors are much weaker: the ^{1}H NMR spectra showed that only a very small amount of sulfate ions were extracted by L^{2a} and almost no extraction was observed for L^{1a} (Figure S8 in the Supporting Information). These results further proved the unique sulfate ion separation behavior of the hexaurea receptor L^3.

In summary, we have developed a tripodal hexaurea receptor for sulfate ions. The receptor is capable of completely encapsulating the anion in a complementary cavity that is protected by aromatic rings, and represents a successful strategy for overcoming the "Hofmeister bias" by taking advantage of a combination of complementarity, the chelate effect, and the hydrophobic effect. With this receptor as a liquid–liquid extractant, almost quantitative extraction of sulfate ions from an aqueous to an organic phase in a recyclable manner has been achieved, and may be promising in the remediation of nuclear waste.

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[15] Crystal data for L^3: $C_{52}H_{60}N_{16}O_{14}S_2$; $M_r = 1197.28$; monoclinic, $C2/c$, $a = 45.443(6)$, $b = 11.8377(14)$, $c = 22.517(3)$ Å, $\beta = 108.109(2)°$, $V = 11513(2)$ Å^3, $T = 293(2)$ K, $Z = 8$, 10101 refl. collected, 3998 unique ($R_{int} = 0.1317$), $R1 = 0.0747$ ($I > 2\sigma(I)$), $wR2 = 0.2371$ (all data). Crystal data for **1**: $C_{82}H_{126}N_{18}O_{17}S_2$; $M_r = 1700.13$; monoclinic, $P2_1/n$, $a = 14.343(5)$, $b = 34.393(12)$, $c = 18.448(6)$ Å, $\beta = 90.524(5)°$, $V = 9100(5)$ Å^3, $T = 293(2)$ K, $Z = 4$, 15944 refl. collected, 6121 unique ($R_{int} = 0.1096$), $R1 = 0.0929$ ($I > 2\sigma(I)$), $wR2 = 0.2590$ (all data). CCDC 784517 (L^3) and CCDC 784518 (**1**) 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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