Fe_4S_4 Clusters Functionalized with Molecular Receptor Ligands

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Cubane-type Fe_4S_4 clusters have been functionalized with the concave dithiol ligands $\mathbf{L^{Xyl}}2H$ and $\mathbf{L^{Ac}}2H$, derived from a diphenylglucoluril-based receptor molecule. In the monomeric cluster compounds $[Fe_4S_4(\mathbf{L^{Xyl}})_2](PPh_4)_2$ (cluster **A**) and $[Fe_4S_4(\mathbf{L^{Ac}})_2](PPh_4)_2$ (cluster **B**), an Fe_4S_4 core is combined with receptor sites for alkali metal ions and aromatic guest molecules. Molecular modelling studies show that the Fe_4S_4 core in compound **B** is tightly encapsulated by its two dithiol ligands, whereas this is not the case for compound **A**. However, unlike the clusters in High-Potential Iron–sulfur Proteins (HiPIP′s), the Fe_4S_4 core in **B** is still accessible to solvent molecules, as has been established by solution electrochemical studies. Both cluster compounds bind alkali metal ions and undergo anodic shifts in their $2^-/3^-$ reduction potentials upon binding of these ions. Electrochemical titrations indicate the complexation of four alkali metal ions per cluster compound. Binding by cluster **B** takes place preferentially at the exterior of the receptor ligands, whereas in the case of cluster **A** the ions also bind to the interior of the receptor. The more open structure of **A** allows the binding of dimethylparaquat **5** [$K_{ass} = (5.6 \pm 0.6) \times 10^3\ m^{-1}$] to this cluster compound. On complexation, the first reduction potential of the guest molecule shifts in the cathodic direction, whereas the reduction potential of the cluster remains unaffected. This observation can be rationalized by assuming that the twofold positively charged guest molecule binds between the aromatic side-walls of the receptor ligands, whereas the one-electron reduced, singly charged positive species is not bound.

Introduction

The properties of prosthetic groups in enzymes are often governed by the protein matrix. Well-known examples are the iron−porphyrin complexes in proteins and enzymes, which can have various properties and functions depending on, e.g., the axial ligation of the central metal ion.[1] Such effects have been studied in great detail in model systems.[2] Another well-studied example is the group of proteins that incorporate an Fe_4S_4 cluster in their active sites. The factors that determine the properties of the cluster are reasonably well understood, largely due to the pioneering model studies by the group of Holm.[3] Fe_4S_4-containing electron-transfer proteins can be divided into two classes, viz. ferredoxins and high-potential iron−sulfur proteins (HiPIP′s), which have low and high reduction potentials, respectively, compared to most physiological redox partners. Of the various oxidation states possible for Fe_4S_4 clusters, ferredoxins cycle between the $[Fe_4S_4(SR)_4]^{2-}$ and $[Fe_4S_4(SR)_4]^{3-}$ states, and HiPIP′s between the $[Fe_4S_4(SR)_4]^{1-}$ and $[Fe_4S_4(SR)_4]^{2-}$ states.[4a] Apart from this, the differences between these two classes are assumed to arise from (i) the number of hydrogen bonds between the peptide backbone and the cluster or its ligands,[4b] (ii) the hydrophobicity of the protein environment of the cluster,[4c] and (iii) the accessibility of the cluster to solvents. The first two aspects have been rather well mimicked with the help of model systems, but model studies on the latter aspect have been much more limited. Okuno and co-workers have described an Fe_4S_4 cluster ligated by a macrocyclic tetradentate thiol ligand.[5] In DMSO solution, the 1^- oxidized state of this cluster, which can be considered as a model of the oxidized form of a HiPIP, was found to be stabilized by the lipophilic macrocyclic ligand. Tabushi et al. have prepared a cluster sandwiched between two cyclodextrin rings.[6] Although this compound showed a remarkable stability in water, no effect of the cyclodextrin moiety on the redox potentials of the Fe_4S_4 cluster was observed. Gorman et al.[7] have shown that increasing the generation of ligands of Fe_4S_4 clusters encapsulated by dendrimers makes the cluster both kinetically and thermodynamically more difficult to reduce. Several half-encapsulated clusters have been reported in the literature, e.g. the 3:1 subsite-differentiated clusters prepared by Holm et al.,[4a−4c] Evans et al.,[8a] and Nolte et al.,[8b−8d] and a tetrathiol-derived cluster based on diphenylglycoluril.[8e][8f] For these clusters, only a slight influence of the ligands on the redox potentials of the Fe_4S_4 core was observed. Apparently, a snug and spherical ligand arrangement is needed to provide a synthetic Fe_4S_4 cluster with a solvophobic environment that stabilizes a higher oxidation state.

In this paper, we describe the synthesis of two bowl-shaped dithiol ligands $\mathbf{L^{Xyl}}2H$ and $\mathbf{L^{Ac}}2H$ (see Chart 1), together with the synthesis and characterization of their Fe_4S_4 cluster compounds **A** and **B**. These ligands were designed with the idea that binding to an Fe_4S_4 cluster would lead to a "closed shell" structure showing interesting redox properties. Figure 1 shows the energy-minimized structure

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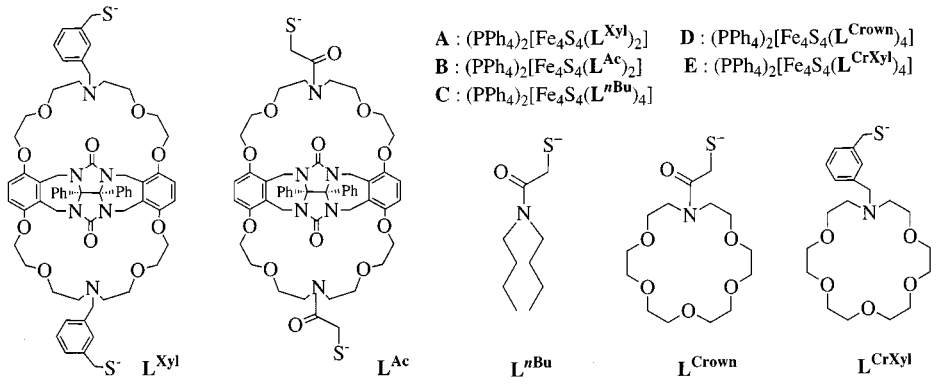


Chart 1

of cluster compound **B**. The space-filling representation (left) suggests that the cluster core (shown in light) is fully encapsulated within the two receptor ligands. Another reason for choosing $L^{Xyl}2H$ and $L^{Ac}2H$ is that these ligands contain receptor sites for binding metal ions and organic guest molecules.[9,10] This opens the possibility of investigating how the electrochemical properties of compounds **A** and **B** change under the influence of such ions and guests.

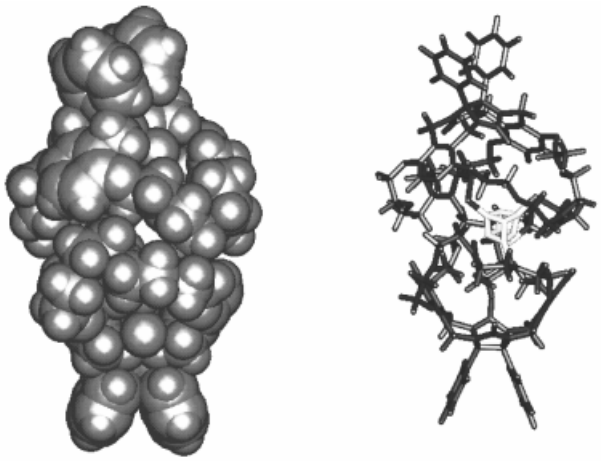


Figure 1. Energy-minimized structure of compound **B**; the ligands are shown in dark, the cluster atoms in light

Results and Discussion

Ligand Synthesis

The ligands $L^{Xyl}2H$ and $L^{Ac}2H$ were synthesized by routes analogous to those that we have used previously for the synthesis of the corresponding crown ether thiols.[9] Starting from the diaza receptor molecule **1a**, alkylation with two equivalents of α-bromo-α′-thioacetyl-*m*-xylene yielded the protected dithiol **2** (see Scheme 1). Removal of the acetate protecting groups was effected by treatment with 3% HCl in methanol. As it was not desirable to subject dithiol $L^{Xyl}2H$ to any purification procedure due to its air sensitivity, the deprotection time was extended to 7 days. TLC analysis indicated that this period was required to ensure complete deprotection of **2**. The overall yield of $L^{Xyl}2H$ was 46%.

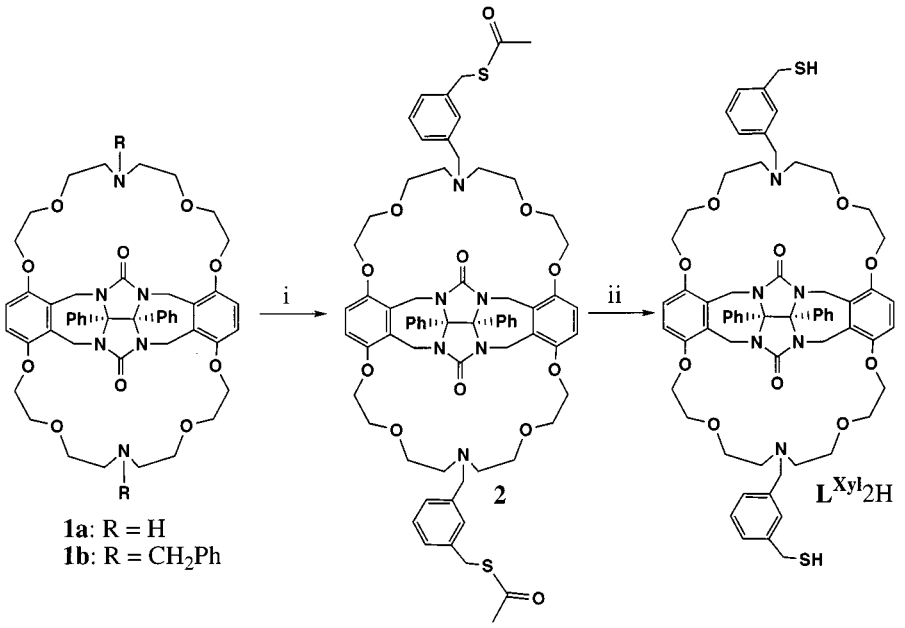
Scheme 2 depicts the synthetic route for the preparation of the dithiol ligand $L^{Ac}2H$. Amidation of receptor **1a** with 2 equivalents of α-chloroacetyl chloride gave compound **3** in reasonable yield (60%). Treatment of this compound with an excess of potassium thiocarboxylate resulted in the formation of the dithioacetate **4**, which was deprotected over a period of 5 days by treatment with 3% HCl in methanol. This procedure gave dithiol $L^{Ac}2H$ in 54% overall yield.

Conformational and Binding Properties of Amidated Receptors 3 and 4

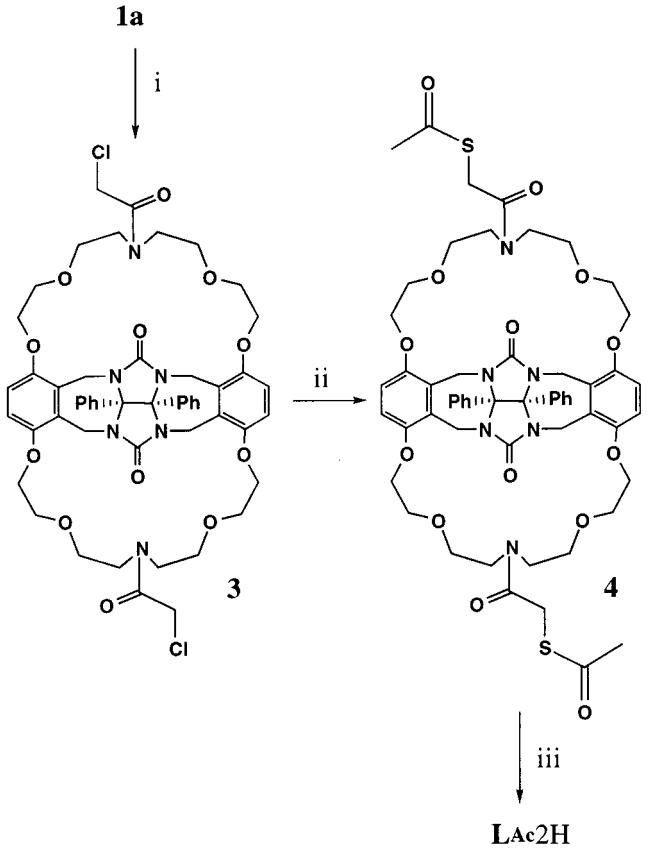
Although chromatographic analysis indicated that the receptor compounds **3** and **4** were pure, ^1H NMR analysis was initially considered to be indicative of the additional presence of other receptor species. Due to conformational restrictions, the protons of the methylene groups connecting the aromatic side-walls to the diphenylglycoluril backbone in **3**, **4**, and $L^{Ac}2H$ behave as AX spin systems.[11] Figure 2 depicts the resonances of the two methylene protons (H_a) in **3** that point upwards in relation to the receptor backbone. The other half of the AX system is obscured by the signals of the crown ether rings. Three doublets for receptors **3** and $L^{Ac}2H$ and two for receptor **4** are observed at around $\delta = 5.7$, instead of just one doublet as anticipated beforehand. Additionally, a multiplet is found for the aromatic wall protons, which normally give a singlet. This splitting is also evident in the ^{13}C NMR spectra of these compounds, where multiple signals are seen for the carbon atoms to which the aforementioned protons are attached.

^1H NMR experiments in which the temperature dependence of the multiple signals was monitored showed that these features can be ascribed to the presence of slowly interconverting conformers of one and the same compound. Increasing the temperature results in coalescence of the multi-doublet signals into one doublet and of the multiplet into one singlet (not shown). The coalescence temperatures were determined as 340 K for receptor **3** and 325 K for receptor **4** (90 MHz).

Apparently, amidation of the nitrogen atoms in the aza-crown ether rings of the basket-shaped receptor molecules



Scheme 1



Scheme 2. Synthesis of dithiol receptor ligand $L^{Xyl}2H$; (i) **1a**, 2 equiv. α-bromo-α′-thioacetyl-*m*-xylene, K_2CO_3, DMF, 40 °C; (ii) 3% HCl/MeOH, N_2

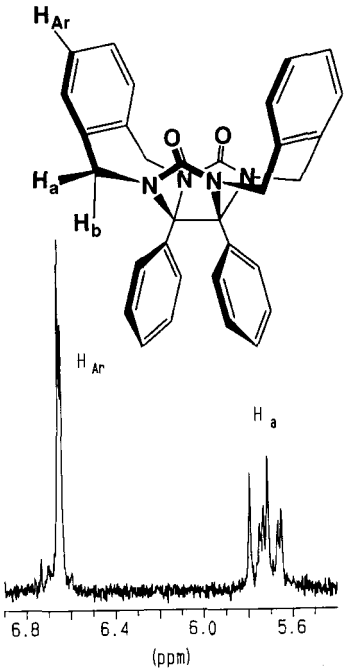


Figure 2. ^1H NMR spectrum of compound **3** in $CDCl_3$ (298 K)

introduces considerable rigidity into these systems. As a result, several conformations can be observed by NMR. Figure 3 shows the different orientations that the amide functions can adopt with respect to the rest of the receptor molecule; the corresponding conformers are proposed to be slowly interconverting on the NMR time scale. The amide functions can point either up or down with respect to the crown ether plane (Figure 3a) and in either position they can again occupy two orientations by rotation about the C(O)−N bond (Figure 3b). The latter two orientations are expected to interconvert more easily than the "up/down" conformers. In the "down" position, the amide groups can be expected to exert a significant influence on the methylene AX spin system, resulting in different signals due to the difference in local environment enforced by these groups. In the "up" position, the amide groups do not have such an influence on this spin system. This explanation accounts for

the observation of three AX doublets with approximate intensity ratios of 1:1:2 in the case of **3**. In a similar way, the amide groups in the "up" positions create a different environment for the aromatic wall protons, whereas in the "down" position no such modification of the environment is induced. This accounts for the observation of multiple resonances for the protons and carbon nuclei of the aromatic side walls. The ease of interconversion of the conformers and, therefore, the spectral characteristics, will depend on the functionalization of the amide group. For this reason, three doublets are observed for the methylene H_a protons of receptors **3** and $\mathbf{L^{Ac}}$2H, as opposed to just two doublets for receptor **4**.

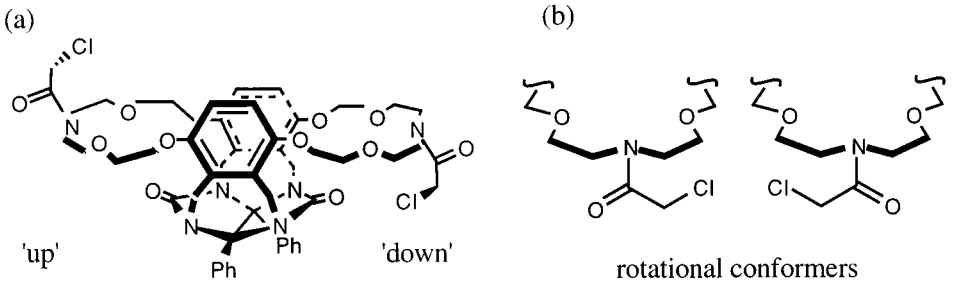


Figure 3. Different conformers of compound **3**

A liquid/liquid (chloroform/water) extraction experiment with potassium picrate revealed that potassium ions are weakly bound by receptor **3** (the association constant K_{ass} was not determined). NMR analysis showed that the presence of these ions did not influence the ratio of the conformers. Addition of resorcinol (1,3-dihydroxybenzene) to solutions of **3** in the presence or absence of K^+ ions resulted in one single AX pattern due to the H_a protons and a singlet due to the aromatic wall protons in the ^{1}H NMR spectrum. Apparently, the aromatic guest molecule is bound by just one of the conformers of **3**. On the basis of CPK models, we tentatively propose this to be the "up/up" conformer. The K_{ass} was determined as 640 ± 10 M^{-1}. This value is significantly lower than the association constants determined for resorcinol and the related receptors **1a** and **1b** (see Scheme 1, K_{ass} = 2000 and 2900 M^{-1}, respectively).[12] This low binding affinity is probably due to the extra energy that is needed to bring the receptor into the conformation for resorcinol binding.

Cluster Synthesis and Characterization

Procedures similar to those described previously[9] for the synthesis of crown ether-derived clusters were used to prepare the clusters $[Fe_4S_4(\mathbf{L^{Xyl}})_2](PPh_4)_2$ (cluster **A**) and $[Fe_4S_4(\mathbf{L^{Ac}})_2](PPh_4)_2$ (cluster **B**) from the two bidentate receptor ligands $\mathbf{L^{Xyl}}$2H and $\mathbf{L^{Ac}}$2H, respectively. Initially, $[Fe_4S_4Cl_4](PPh_4)_2$ was used as the starting material for the synthesis of cluster **A**. A DMF solution of this compound was slowly added to a dilute DMF solution (< 1 mM) containing two equivalents of the ligand $\mathbf{L^{Xyl}}$2H and four equivalents of $(NBu_4)OH$ as a base. The progress of the reaction was monitored by DPV analysis of aliquots withdrawn from the mixture. Besides the formation of the desired product, characterized by a reductive peak at −1.74 V, an unknown by-product was also observed ($E_{p,c}$ = −1.36 V). At the point where DPV analysis indicated no further change in the composition of the reaction mixture, the products were isolated by means of precipitation followed by filtration. The by-product was removed by washing with CH_2Cl_2. NMR analysis showed that the desired Fe_4S_4 product was isolated as the tetrabutylammonium salt, probably because this salt is less soluble than the tetraphenylphosphonium salt. After isolation and washing with CH_2Cl_2, the product obtained was indeed found to be poorly soluble; it did not dissolve in DMF and only very poorly in DMSO. Attempts to prepare cluster **A** through in situ synthesis in an electrochemical cell failed. An unidentified precipitate was formed, which might have originated from the excess tetrabutylammonium salt present as the supporting electrolyte. These procedures either failed to yield the desired product or produced it in a form unsuitable for further analysis. $[Fe_4S_4(S\mathit{t}Bu_4)](PPh_4)_2$ was therefore used as the starting material in all subsequent experiments. The fact that no base is needed with this starting material was thought to be favourable for the syntheses of the clusters **A** and **B**. Ligand-exchange reactions were performed by applying a dynamic vacuum after rapid mixing of dilute DMF solutions of the *tert*-butyl thiolate cluster with two equivalents of the appropriate ligand. After six hours, DPV analysis was indicative of complete conversion into a single product in each case. Both cluster compounds were isolated as black, shiny solids. We were unable to grow crystals from the isolated materials; the use of counterions known to favour crystallization of related compounds, i.e. $(NBu_3Bzl)^+$,[13] was not successful in the present case.

The newly synthesized cluster compounds were first characterized by electrochemical means. Our earlier experience with crowned cluster compounds showed this to be an excellent method for examining the formation of the clusters as well as their redox chemistry.[9] Due to the sensitivity of the CV and DPV techniques, it was also anticipated that any formation of soluble oligomeric or polymeric materials would be detectable in this way.

Table 1 lists the electrochemical characteristics of the $2^-/3^-$ reduction of cluster compounds **A** and **B** in DMF solution. The half-wave potentials ($E_{1/2}$) for reduction of these compounds resemble the values determined for related crown ether-functionalized clusters, e.g. **D**.[9] On CV ana-

lysis, a chemically reversible reduction process was observed for cluster **A**, whereas this process was found to be electrochemically quasi-reversible due to a relatively slow electron-transfer rate. For cluster **B**, the opposite behaviour was found, viz. an electrochemically reversible but chemically quasi-reversible reduction (see Figure 4). These results are indicative of significantly better defined redox processes for clusters **A** and **B** than for the previously studied crowned cluster compounds. Apparently, the fact that the cluster cores in **A** and **B** are ligated by bidentate rather than monodentate ligands prevents the occurrence of irreversible redox chemistry involving thiolate ligands not coordinated to the cluster core. The peak separations suggested that no oligomeric or polymeric materials had been formed, as much larger separations would have been expected if this had been the case. For neither of the two cluster compounds was a reversible $2^-/1^-$ oxidation process observed.

Table 1. Electrochemical characteristics of the $2^-/3^-$ reduction of cluster compounds **A** and **B** in DMF

[a]	Electrode	**A** Pt	PGE	**B** Pt	PGE
CV	$E_{1/2}$ (V)	−1.78	−1.75	−1.60	−1.64
	ΔE_p (mV)	100	90	70	60
	i_b/i_f	1.0	−[b]	0.59	−[b]
DPV	E_p (V)	−1.74	−1.74	−1.62	−1.61
	$W_{1/2}$ (mV)	107	160	140	108

[a] Potentials are given against the Fc/Fc^+ couple in the same solvent. PGE = Pyrolytic graphite edge. − [b] Due to the large capacitative current these values could not be determined.

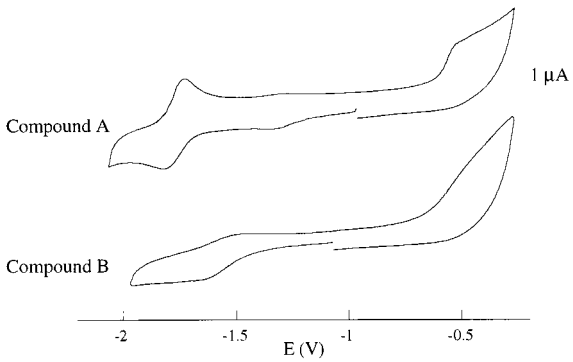


Figure 4. Cyclic voltammograms of compounds **A** and **B** in DMF (reductive scans, Pt working electrode)

Earlier studies by our group on semi-encapsulated cluster compounds showed that the use of graphite electrodes was advantageous in their electrochemical analysis.[7,8] In the present case, however, a graphite working electrode instead of a platinum one was not found to be beneficial. Instead, lower current responses were found, which complicated the analysis. No significant changes in peak potentials were observed. Moreover, compounds **A** and **B** could be electrochemically analyzed without the need for Ba^{2+} ions as promoting or modulating species. This clearly sets these compounds apart from their semi-encapsulated analogues[8b−8f] and suggests that the cluster cores in **A** and **B** are surrounded by the ligands in such a way that no effective dipole moment exists in these complexes. These results also confirmed that complexes **A** and **B** were isolated as monomeric materials.

It was hoped that by surrounding the Fe_4S_4 cluster with a large spherical ligand a solvophobic environment around the cluster core might be created and that the redox centre would be shielded from the electrode. However, the electrochemical properties of **A** and **B**, as outlined above, do not suggest that this shielding is effective for either of the two compounds. This is not unexpected for **A** because the xylylene spacers between the cluster and the receptor sites in this compound are relatively long, exposing the redox site to the solvent and to the electrode surface. On the other hand, modelling studies suggested that compound **B** should be able to adopt a compact and closed structure (see also Figure 1). As such a structure was seemingly not present in DMF, we decided to use DMSO as the solvent for the electrochemical measurements. The choice of DMSO was based on NMR studies (vide infra), which indicated that the Fe_4S_4 core of **B** is tightly embraced by its ligands in this solvent. For comparison purposes, the electrochemical properties of two structurally related cluster compounds were also studied in this solvent. These compounds bear dibutylamine (compound **C**) and monoaza-18-crown-6 acetyl thiolate ligands (compound **D**), respectively (see Chart 1).[9]

For the dibutylamine thiolate functionalized compound **C**, a reversible reduction process was observed under normal conditions (not shown). A small pre-wave was visible for the $2^-/3^-$ reduction process ($E_{1/2}$ = −1.52 V), which arises either because of coordination of solvent molecules to the cluster core or due to absorption of the reduced species onto the electrode. For the crown ether functionalized compound (cluster **D**), the current response was rather low and again a pre-wave associated with the reduction of the cluster was observed. The addition of $Ba(ClO_4)_2$ considerably improved the current response and also induced an anodic shift in the reduction potential ($E_{p,red}$ = −1.58 V). The origins of these effects have been discussed previously[9] and originate from metal ion binding by the crown ether ligands. For compound **B**, a poorly defined voltammogram was obtained, showing a very faint reductive feature at a similar potential as found for compound **D** in this solvent. Addition of $Ba(ClO_4)_2$ again led to an increased current response and an anodic shift in $E_{p,red}$. In this case, an irreversible reduction was observed at around −1.42 V, a potential similar to that measured for the pre-wave of compound **D**. For neither of the three cluster compounds was a clear, reversible oxidation process observed under any of the investigated conditions.

The results of the aforementioned experiments show that the increasing ligand size on going from cluster compound **C**, to **D**, and then **B** leads to increasingly hampered electron-transfer from the cluster compound to the electrode in DMSO. Furthermore, shielding of the cluster core by the large receptor ligand does not in this case lead to stabilization of higher oxidation states of the cluster. In previous studies, Okuno et al.[5] showed that their cluster compound, in which the cluster is coordinated by a sterically encum-

bered macrocyclic tetrathiolate ligand, undergoes a reversible $2^-/1^-$ transition in DMSO at a potential significantly more positive than that of several model compounds.[5] Data in DMF were not reported for this particular compound. Normally, higher oxidation states of iron–sulfur clusters would be expected to be stabilized in apolar solvents and destabilized in polar solvents such as DMF or DMSO.[14] Okuno and co-workers concluded that the compact structure of their compound in DMSO leads to stabilization of the 1^- oxidation state through the creation of a solvophobic environment. Although a similar behaviour might be expected in our system, the stabilization of a higher oxidation state is apparently not possible. This may be due to the rather polar nature of the crown ether fragments in our receptor ligands or due to the fact that the cluster core is still accessible to solvent molecules in spite of the tight ligand encapsulation.

The absorption spectra of compounds **A** and **B** were found to correlate very well with the spectra of the structurally related crown ether compounds (see Table 2).[9] This confirms that the Fe_4S_4 cubane core is retained in the new compounds. It also indicates that the local environment of the thiolate sulfur atoms[4c] in **A** and **B** is similar to that in the crown ether analogues. The ligand-to-metal charge-transfer (LMCT) absorption bands at ca. 400 nm in Fe_4S_4 clusters are known to undergo a blue shift in solvents of high ε.[15] Similar blue shifts have been observed for cluster compounds bearing sterically encumbered thiolate ligands, which were additionally shown to display reversible $2^-/1^-$ transitions in CV and were therefore presented as HiPIP

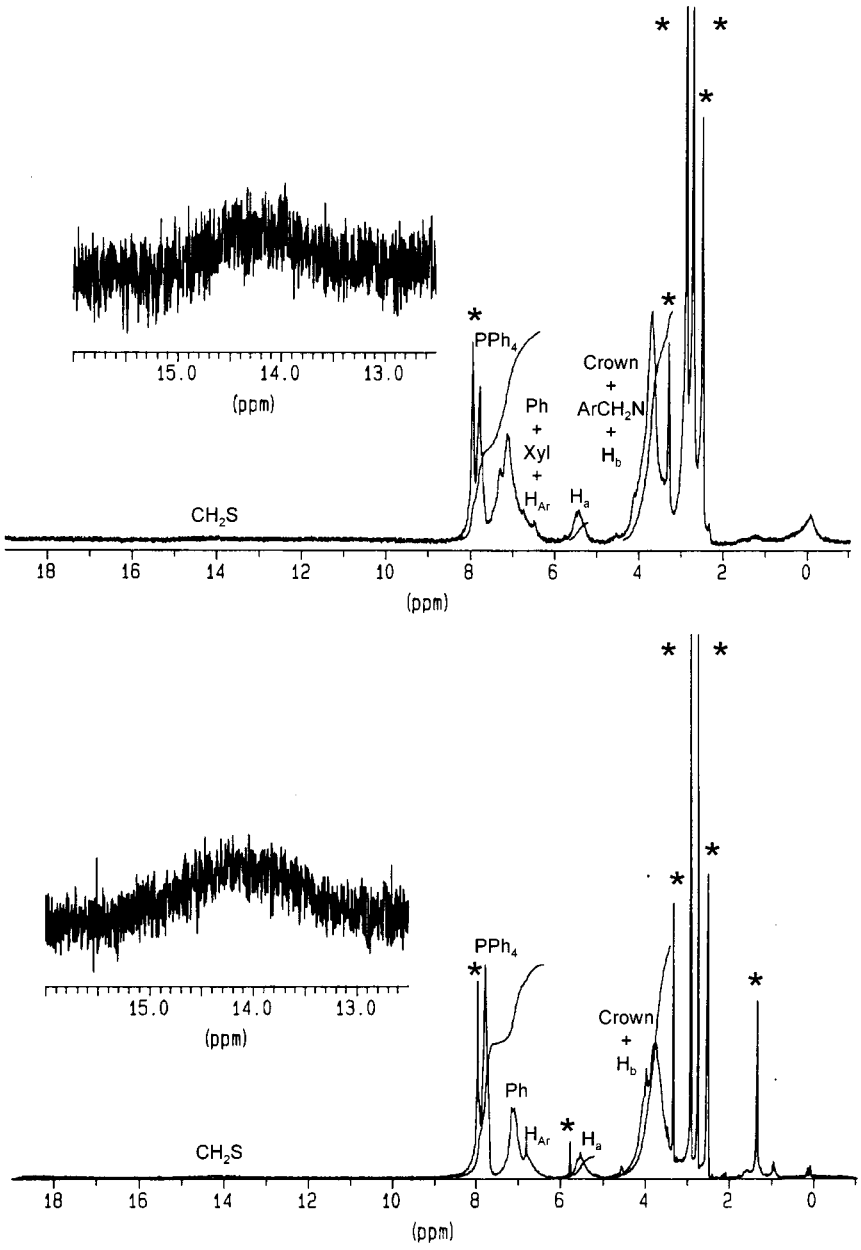


Figure 5. ^{1}H NMR spectra of cluster compounds **A** (top) and **B** (bottom) in [D_6]DMSO

models.[16] The fact that no such blue shifts are observed for compounds **A** and **B** is in line with their electrochemical behaviour (no reversible $2^-/1^-$ transitions).

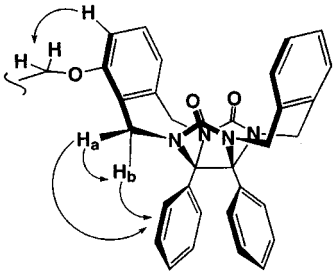
Table 2. UV/Vis data of cluster compounds in DMF

Compound	λ_{max}
A	290, 420, 620 (sh)
$[NBu_4]_2[Fe_4S_4(SBzl)_4]$	300 (sh), 420
B	295, 340 (sh), 415, 622 (sh)
C	301, 415, 620 (sh)
D	300, 410, 660 (sh)

The ^{1}H NMR spectra of compounds **A** and **B** exhibit the typical features of Fe_4S_4 thiolate clusters,[9] i.e. large chemical shifts and broadened peaks (see Figure 5). The resonances of the methylene protons adjacent to the thiolate sulfur atoms are observed as broad signals at around $\delta = 14$ (see Table 3 for details). The chemical shifts of these signals were found to increase linearly with temperature in the region 298−348 K (not shown). The other proton signals of **A** and **B** are also somewhat broadened, suggesting either that these protons lie in the proximity of a paramagnetic centre or that the complexes adopt different conformations that are in rapid exchange on the NMR time scale. A complete assignment of the peaks was performed in the case of compound **B** by means of a 2D-COSY experiment, the coupling constant of the $ArCH_2N$ protons of the diphenylglycoluril unit being determined by 2D-DQF-COSY experiments (see Experimental Section).

In cluster compound **D**, which, like compound **B**, also bears α-mercaptoacetyl ligands, the crown ether ligands have a somewhat restricted conformational freedom, as was concluded from the appearance of two discrete and relatively sharp signals due to the CH_2S protons.[9] Such an inequivalence in chemical shift is not observed for the CH_2S protons in **B**. Instead, the signals are broad, the width at half peak height being 1.4 ppm as compared to 0.4 ppm in the case of compound **D**. This broadening might be indicative of the superposition of several peaks, implying that two or more CH_2S groups in **B** have somewhat different orientations with respect to the cluster core, and hence that the ligation of the cluster core in **B** is not symmetrical. Moreover, some flexibility of the ligands with respect to the cluster core leading to slowly exchanging conformers might be possible. Similar considerations probably apply to compound **A**, the structure of which can be expected to be much more flexible than that of **B**.

Due to the broadening of the signals in the one-dimensional ^{1}H spectrum, it was not possible to establish whether the ligands of compound **B** existed in more than one conformation. The solution structure of compound **B** was therefore studied in more detail by means of a 2D-NOESY experiment. Part of the 2D-NOESY spectrum of compound **B** is shown in Figure 6. Several contact cross-peaks are apparent, first and foremost between the two $ArCH_2N$ protons of the diphenylglycoluril backbone themselves and between one of these protons (H_a) and the protons (PhH′s) of the phenyl rings at the bottom of the receptor ligand. In addition, an interaction is in evidence between the aromatic wall protons and the methylene protons in the crown ether part of the ligand. Most of these through-space interactions were expected on the basis of earlier NMR studies on diphenylglycoluril-based receptor molecules,[11] but the H_a−PhH interaction is new. 2D-NOESY experiments on compound **3** and cluster compound **A** showed no spatial proximity of these protons.



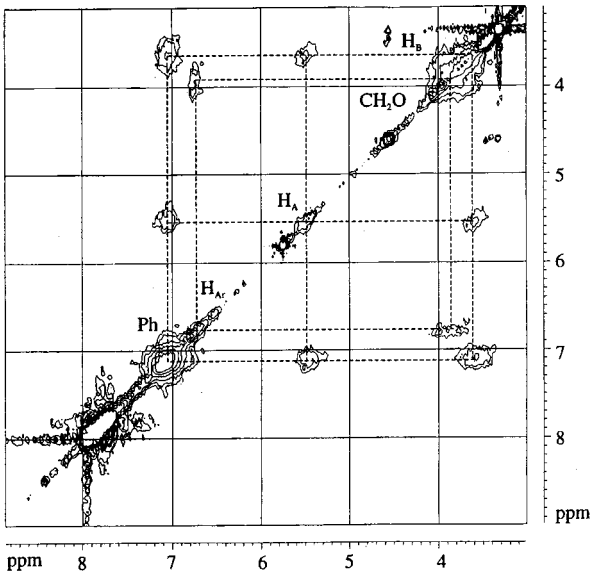


Figure 6. 2D-NOESY spectrum of cluster compound **B** in $[D_6]$DMSO

All the protons for which cross-peaks are observed (except the aforementioned H_a and PhH′s) can be assumed to lie in close proximity to one another on the basis of crystallographic analyses of two related receptor molecules[17] and of several other clip molecules.[18] Conformational isomers

Table 3. ^{1}H NMR temperature-dependence of isotropically shifted ligand signals in cluster compounds **A** and **B** in $[D_6]$DMSO

		Free ligand (δ/ppm)	Cluster (δ/ppm)	ΔH^{iso} (ppm)	$\Delta H^{iso}/T$ (Hz/K)
A	CH_2S	4.0	14.3	−10.3	−5.96
B	CH_2S	4.1	14.1	−10.0	−5.18

can be obtained by "flipping" the aromatic walls, as has been observed previously for receptor molecules bearing naphthalene walls.[19] Such a "flipping" process might explain the close proximity of H_a and the PhH′s, but it has never been observed for clip molecules with benzene walls. Examination of CPK models of compound **B** suggests that a different type of conformational rearrangement may occur in the backbone of ligand $\mathbf{L^{Ac}}$ upon coordination to an Fe_4S_4 cluster. In order to allow the two thiol groups of $\mathbf{L^{Ac}}$ to reach the cubane cluster, the receptor ligands have to adopt a bent conformation (see Figure 7). This leads to conformational stress in the two crown ether rings, which can be overcome by pushing the aromatic walls somewhat closer together; the latter process can be accomplished through rotation of the $ArCH_2N$ methylene groups. This, in turn, places these methylene groups in closer proximity to the phenyl rings at the rear side of the diphenylglycoluril framework. Overall, this would result in a more snug fit of the bidentate ligands around the cluster core.

The promoting effects of the various alkali metal ions, as evaluated from the increase in peak current (i_p) in DPV, are distinctly different for compounds **A** and **B** (not shown). For all the metal ions tested, a distinct promoting effect was seen in the case of **A**, but for **B** these effects were only observed with metal ions that also showed a significant modulating effect.[20] Except in the case of Li^+, addition of the first equivalents of a metal ion to compound **A** resulted in an increased current response in both DPV and CV, which

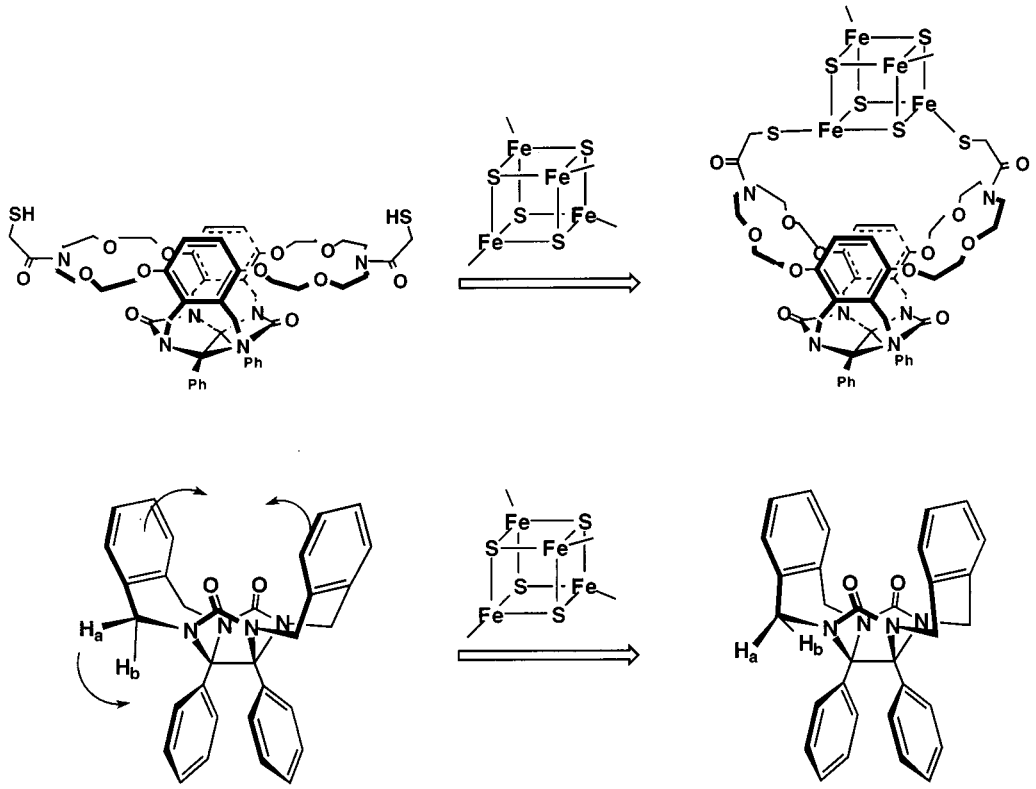


Figure 7. Proposed conformational rearrangement of the crown ether rings (top) and the aromatic walls (bottom) of the receptor ligands upon coordination to the cubane core in **B**

Electrochemical Response Towards Metal Ions

Compounds **A** and **B** each contain a redox-active site that lies in close proximity to two receptor sites for charged guests. It was therefore of interest to study the electrochemical behaviour of **A** and **B** towards alkali and alkaline earth metal ions. Figure 8 shows the titration curves of compound **A** with Na^+ and Ba^{2+} ions as followed by DPV and CV. The changes in the peak potentials (E_p′s) for compounds **A** and **B** in DPV upon the addition of various metal ions are listed in Table 4. These changes are all in the anodic direction, showing that reduction of the cluster cores is facilitated by the addition of metal ions. This also indicates a higher affinity of the reduced clusters for these metal ions as compared to the oxidized clusters. The addition of metal ions was found to have little if any influence on the chemical and electrochemical reversibility of the $2^-/3^-$ reductions of **A** and **B**, which was already satisfactory in the absence of any additive (vide supra).

suggests binding of the metal ions to this cluster compound (see Figure 8a and 8b, respectively, for Na^+). Figure 9 shows the titration curves, where E_p and i_p are plotted against the amount of metal ion added to compound **A**. For **B**, an increased current response was only observed with Ba^{2+} ions (titration curves not shown). We propose that the increased current responses seen in CV and DPV are not the result of electrode modifications (metal ion absorption), but are due to the fact that the overall negative

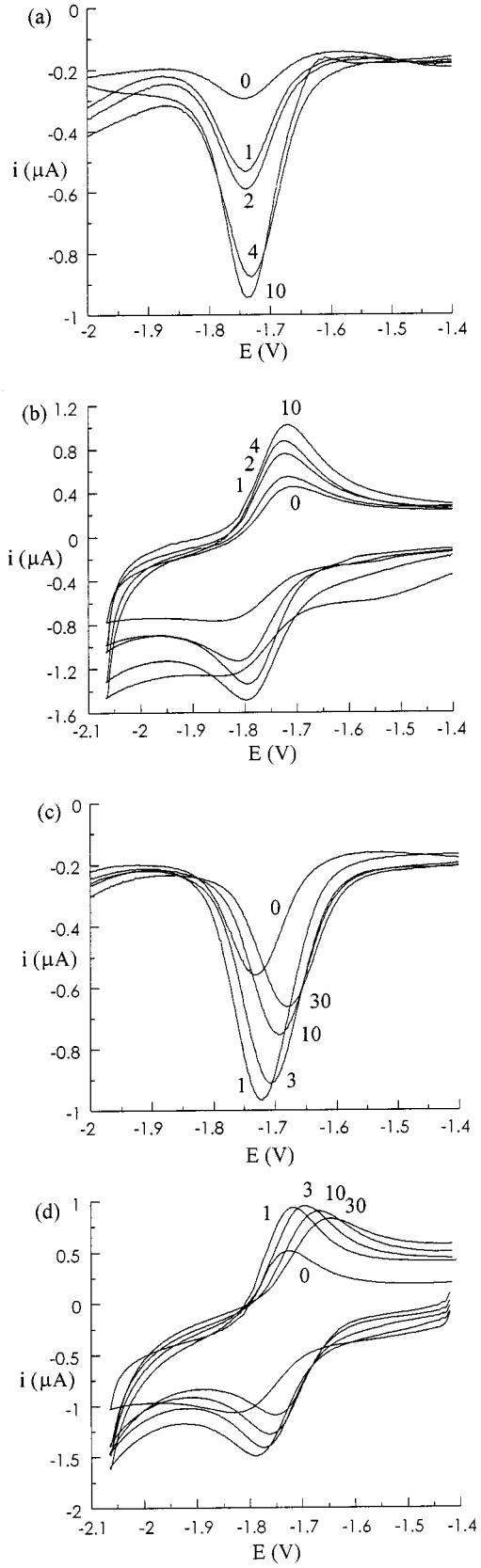


Figure 8. (a) DPV and (b) CV titrations of compound **A** with Na^+ ions; (c) DPV and (d) CV titrations of compound **A** with Ba^{2+} ions; numbers refer to the equivalents of metal ions per cluster

Table 4. Changes in DPV peak potentials (mV) of compounds **A** and **B** upon addition of 10 equivalents of various metal ions in DMF

	A[a]	**B**[a]
Li^+	(0)	(10)
Na^+	10 (30)	(0)
K^+	10 (20)	(20)
Mg^{2+}	0 (20)	(40)
Ba^{2+}	40 (50)	110 (140)

[a] The value for an excess of metal ions is given in brackets.

charge of the cluster is reduced or even becomes positive upon the binding of metal ions. The fact that no increase in current response is observed when Li^+, Na^+, or K^+ ions are added to compound **B** suggests that this receptor compound has a much lower affinity for these metal ions than compound **A**.

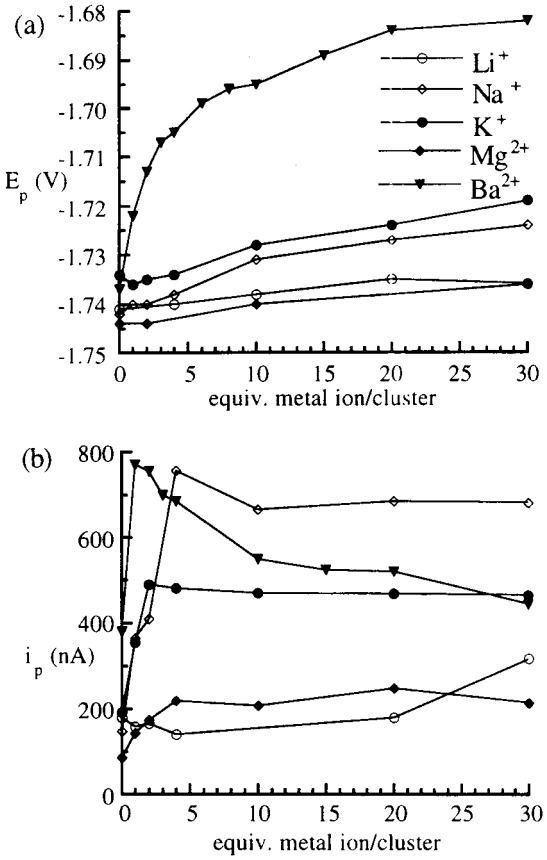


Figure 9. Titration of compound **A** with various alkali and alkaline earth metal ions as followed by DPV; (a) changes in E_p, (b) changes in i_p

The changes in E_p for compound **A** are much smaller than those observed for the related crown ether cluster compound **E**.[9] Nevertheless, the trend in metal ion dependence is the same. In the case of the crown ether compound, the selective response was shown to stem from electrostatic forces, mediated in a "through-bond" manner by a putative "lariat-type" interaction. In the case of compound **A**, the response appears to be mainly determined by the affinities of the metal ions for the crown ether units of the ligands.

The metal ion binding properties in chloroform solution of the central framework of **A**, viz. the diphenylglycoluril-based basket compound **1a**, have been determined previously.[21] It was shown that Li^+, Na^+, and K^+ are bound to **1a** with K_{ass}'s of 0.38×10^6 M^{-1}, 0.83×10^6 M^{-1}, and 1.9×10^6 M^{-1}, respectively. The binding of these metal ions takes place in a 1:1 clamshell fashion.[21] The binding constants for Mg^{2+} and Ba^{2+} can be expected to be somewhat higher than those for Li^+ and K^+, respectively, taking into account the sizes and charge densities of these ions. Given the high binding affinities of the basket molecule **1a** for alkali metal ions, larger changes in E_p than those listed in Table 4 might have been expected for compound **A**. Apparently, the metal ions are not bound in close proximity to the redox centre in **A**. This is confirmed by the fact that in DPV and CV compound **A** displays continuous wave rather than multi-wave behaviour. The clamshell binding mode proposed for **1a** seems to be unlikely for **A** because the E_p titration curve with Ba^{2+} suggests that this cluster compound binds four metal ions rather than two. Each crown ether fragment in **A** seemingly takes up one metal ion. The metal ions can either "nestle" in the cavity of the receptor ligand ("top" binding) or bind at its exterior ("bottom" binding, see Figure 10). Examination of CPK models showed that the four oxygen atoms and nitrogen atom in each of the aza crown ether rings, together with one of the carbonyl groups from the ligand backbone, form a circular array of donor atoms with an internal diameter comparable to that of 18-crown-6. Analysis of the i_p titration curves suggests that compound **A** has a similar metal ion binding profile as 18-crown-6, *viz.* $Li^+ < Mg^{2+} < Na^+ < K^+ < Ba^{2+}$, which also explains the modulating effects observed for compound **A**.

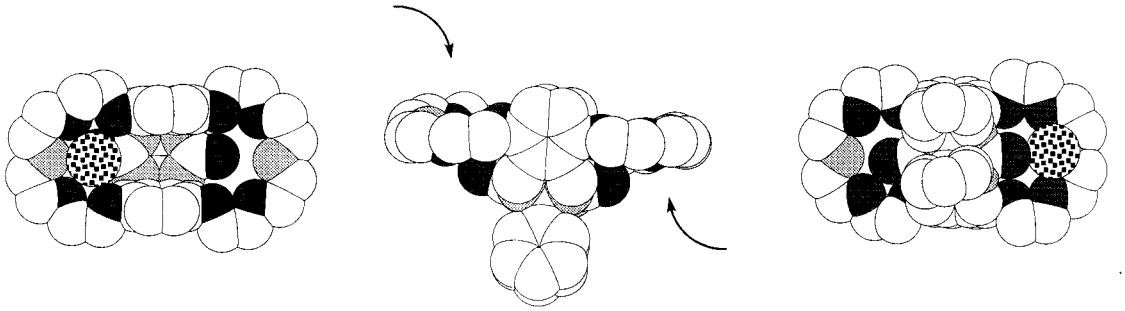


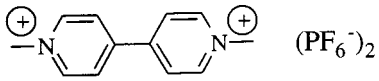
Figure 10. Proposed binding modes of metal ions by compound **A**

The modulation characteristics of compound **B** appear to be determined by similar, crown ether dependent binding factors. Due to the fact that the nitrogens in its crown ether rings are amidated, the binding characteristics of **B** are different from those of compound **A**. Furthermore, as there is less free space between the cluster core and the ligands in **B** than in **A**, the binding of metal ions can be expected to take place preferentially at the exterior (bottom side) of the cavities, as shown in Figure 10 (right). The absence of any increase in current response with Li^+, Na^+, and K^+ ions suggests that the affinity of compound **B** for these cations is low, probably due to the aforementioned amidation of the nitrogens of the crown ether rings. However, as a result of the smaller spacer groups, any bound metal ion will be closer to the cluster core in **B**. Electrostatic forces will therefore be more dominant in compound **B** than in **A**. This may explain the large electrochemical effect of Ba^{2+} ions compared to, e.g., Li^+ and Mg^{2+} ions in the case of the former compound.

Binding of Aromatic Guests by Cluster Compound A

The results presented in the previous sections suggest an open and relatively flexible structure for cluster compound **A**, with binding sites that are accessible to guests. In order to probe this accessibility, the binding of aromatic molecules by compound **A** was also investigated. Diphenylglycoluril receptors are known to bind various aromatic guest molecules in nonpolar solvents such as chloroform and dichloromethane.[12] For solubility reasons, the binding properties of compound **A** were evaluated in DMF. DPV titrations of **A** with 1,2-dinitrobenzene, 2,3-dicyanohydroquinone, and 2,3-dibromohydroquinone showed that the redox potential of the cluster was not affected by these additives. Separate UV/Vis titrations using compound **A** and receptor molecule **1a** revealed that in DMF neither of these host compounds binds the aforementioned guest molecules, in accordance with the outcome of the DPV experiments. Addition of *o*-phenylenediammonium dipicrate to the DMF solutions of **A** was found to result in degradation of the complex, probably due to protonation of the cluster core.

More recently, it has been shown that paraquats (1,1′-disubstituted 4,4′-bipyridinium salts) are very strongly bound by basket-shaped receptors based on diphenylglycoluril, even in polar solvents such as acetonitrile and methanol.[17b] Titration of model compound **1b** (Scheme 1) with dimethylparaquat **5** (Chart 2) in DMF resulted in the development of a band at 402 nm in the UV/Vis spectrum, indicating the formation of a charge-transfer (CT) complex between these two components.[22] The binding constant was determined to be $K_{ass} = 155 \pm 3$ M^{-1}. This value is considerably lower than the binding constant measured for this host–guest combination in 1:1 (*v*/*v*) chloroform/methanol, *viz.* $K_{ass} = 6000$ M^{-1}.[17b]



5

Chart 2

The binding of paraquat **5** by compound **A** was proven by electrochemical titration experiments. Figure 11a depicts the CV titration of **5** with **A**; it shows the two reversible reduction steps for **5** at −0.89 and −1.29 V, and the reduction of **A** at −1.78 V. Clearly, the first reduction of **5** is influenced by the host compound **A**, as was also indicated by DPV (see Figure 11b, where the change in $E_{p,red}$ is plotted against twice the host concentration). The second reduction potential of **5** and the reduction potential of **A** are not affected.

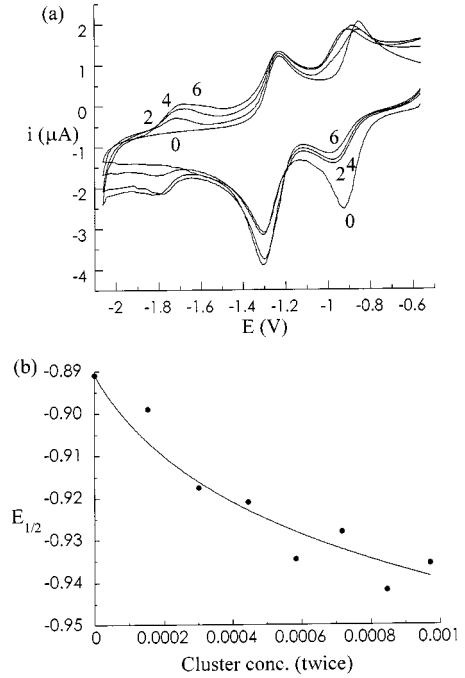


Figure 11. (a) CV titration of compound **5** with **A**, and (b) the change in E_p for the first reduction of **5** as function of twice the cluster concentration; for an explanation, see text; numbers in (a) refer to the number of molar equivalents of clusters relative to **5**

From these observations, it was concluded that only the twofold positively charged paraquat species is bound by **A**. The single positively charged and neutral species apparently have no affinity for this compound. This also explains why the reduction potential of **A** is unaffected by **5**; only a small increase in ΔE_p is observed. Binding stabilizes the dicationic form of **5** and makes it more difficult to reduce this compound, resulting in the observed anodic changes in $E_{1/2}$. We analyzed these changes, assuming the formation of a 2:1 paraquat−host complex, with the help of Equation (1), where $E_{1/2}$ is the observed half-wave potential, $E_{1/2}^{free}$ the half-wave potential of **5** without any additive, and [H] the concentration of the host compound.

$$E_{1/2} = E_{1/2}^{free} - 0.059 \log (1 + K_{ass}[H]) \quad (1)$$

Assuming that the two binding sites in **A** behave completely independently, the actual host concentration was taken as twice the concentration of cluster compound **A**. With the help of Equation (1), the curve in Figure 11b was obtained, from which a binding constant of $K_{ass} = (5.6 \pm 0.6) \times 10^3$ M^{-1} was calculated.

In separate experiments, we also added $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ to paraquat **5**. This was shown to have no effect on the electrochemical behaviour of **5**. It is therefore concluded that the combination of a concave binding site and a negatively charged cluster fragment significantly enhances binding of paraquat **5** to basket-shaped receptors derived from diphenylglycoluril, viz. its binding constant increased from $K_{ass} = 155$ M^{-1} in **1b** to $K_{ass} = 5.6 \times 10^3$ M^{-1} in cluster compound **A**.

Conclusions

The electrochemical and spectral properties of the compounds **A** and **B** strongly suggest that these compounds, as isolated, are monomeric and contain an intact Fe_4S_4 cubane core. The formulation of **A** and **B** as $[Fe_4S_4(\mathbf{L^{Xyl}})_2](PPh_4)_2$ and $[Fe_4S_4(\mathbf{L^{Ac}})_2](PPh_4)_2$ therefore seems to be justified. NMR studies have shown compound **B** to have a relatively compact structure, in which the cluster is encapsulated by the concave receptor ligands. The extent of encapsulation is not such that it creates a solvophobic environment similar to that in Fe_4S_4 cluster containing proteins of the HiPIP class.

The structure of compound **A** was found to be less compact than that of compound **B**, implying that the binding sites of the receptor ligands in **A** are more accessible to guest molecules than those in **B**. The electrochemical responses of the two compounds towards alkali and alkaline earth metal ions indeed indicated that compound **A** has an "open" structure while compound **B** has a more or less "closed" structure. The cavity-forming ligands of **A** are also capable of binding a dicationic paraquat guest, but not its reduced forms. This binding interaction was found to influence the redox properties of the guest molecule.

Experimental Section

For a detailed description of the materials and methods used, the reader is referred to the related paper.[9]

Additional methods: 2D NMR spectra (COSY and NOESY) were recorded on a Bruker WM-200 instrument. In the NMR titration experiments, the changes in the chemical shifts of the host and guest molecules were monitored at varying host and at constant guest concentrations. − For electrochemical experiments, an Ag/AgCl reference electrode and 0.2 M tetrabutylammonium perchlorate supporting electrolyte solution were used, with DMSO as the solvent. − Calculations were performed on Silicon Graphics Challenge and Silicon Graphics Indigo II workstations using the QUANTA molecular modelling package with the CHARMm 3.3 force field. The Fe_4S_4 core was fixed and only the attached basket ligand structure was minimized.

2a,8,9,12,13,14,15,17,18,25,26,29,30,31,32,34,35,38b-Octadecahydro-2a,38b-diphenyl-13,30-1*H*,4*H*-6,37:20,23-dietheno-2,22:3,21-dimethano-5*H*,11*H*,28*H*,38*H*-7,10,16,19,24,27,33,36-octaoxa-2,3,4a,13,30,38a-hexaazacyclopenta[*cd*]cyclotetratriacont[*g*]azulene-1,4-dione (1a): This compound and derivative **1b** were synthesized according to a previously published procedure.[23]

2a,8,9,12,13,14,15,17,18,25,26,29,30,31,32,34,35,38b-Octadecahydro-2a,38b-diphenyl-13,30-bis(α-thioacetyl-*m*-xylyl)-1*H*,4*H*-6,37:20,23-dietheno-2,22:3,21-dimethano-5*H*,11*H*,28*H*,38*H*-7,10,16,19,24,27,33,36-octaoxa-2,3,4a,13,30,38a-hexaazacyclopenta[*cd*]cyclotetratriacont[*g*]azulene-1,4-dione (2): To a solution of **1a** (328 mg, 0.380 mmol) in DMF (15 mL) containing a small amount of K_2CO_3, a solution of α-bromo-α′-thioacetyl-*m*-xylene (195 mg, 0.75 mmol) in DMF (5 mL) was added dropwise. The resulting mixture was stirred overnight at 40 °C under an N_2 atmosphere. After removal of the solvent in vacuo, the residue was taken up in CH_2Cl_2 (40 mL) and the resulting solution was washed twice with brine and dried over $MgSO_4$. Purification by flash chromatography (silica, $CHCl_3$/MeOH/TEA, 96:3:1, *v*/*v*) yielded 425 mg (91%) of **2** as a white powder; m.p. 186 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.31 [s, 6 H, C(O)CH_3], 2.88 (t, *J* = 5.7 Hz, 8 H, NC$H_2$$CH_2$O), 3.69−4.15 (m, 36 H, CH_2O, NC*H*HAr, NCH_2ArCH_2S), 5.67 (d, *J* = 16.1 Hz, 4 H, NCH*H*Ar), 6.73 (s, 4 H, ArH), 7.11 (s, 10 H, PhH), 7.31 (m, 8 H, ArH). − FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3057, 3029 (ArH), 2922, 2869 (CH_2), 1711 (C=O, urea), 1690 (C=O, thio ester), 1459, 1426 (CH_2), 1131, 1017 (COC), 770, 603 (Ar). − FAB-MS; *m*/*z*: 1233 [M + 1]$^+$. − No satisfactory elemental analysis could be obtained for this compound.

2a,8,9,12,13,14,15,17,18,25,26,29,30,31,32,34,35,38b-Octadecahydro-2a,38b-diphenyl-13,30-bis(α-thio-*m*-xylyl)-1*H*,4*H*-6,37:20,23-dietheno-2,22:3,21-dimethano-5*H*,11*H*,28*H*,38*H*-7,10,16,19,24,27,33,36-octaoxa-2,3,4a,13,30,38a-hexaazacyclopenta[*cd*]cyclotetratriacont[*g*]azulene-1,4-dione (L^{Xyl}2H): A solution of **2** (195 mg, 0.158 mmol) in methanol (10 mL) containing 3% HCl was stirred under N_2 atmosphere for 7 days at ambient temperature. Thereafter, TLC analysis showed one single, nitroprusside-positive spot. The reaction mixture was then partitioned between CH_2Cl_2 (20 mL) and water (10 mL). After neutralization with saturated aqueous $NaHCO_3$ solution, the organic layer was separated, washed with further water, and dried over $MgSO_4$. After removal of the solvent in vacuo, the desired product (90 mg, 50%) was obtained as a white powder. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.75 (t, *J* = 7.54 Hz, 2 H, SH), 2.89 (br. s, 4 H, NC$H_2$$CH_2$O), 3.62−4.08 (m, 36 H, CH_2O, NC*H*HAr, NCH_2ArCH_2, ArCH_2S), 5.60 (d, *J* = 16.1 Hz, 4 H, NCH*H*Ar), 6.63 (s, 4 H, ArH), 7.04 (s, 10 H, PhH), 7.19−7.32 (m, 8 H, ArH). − FAB-MS; *m*/*z*: 1149 [M + 1]$^+$. − No satisfactory elemental analysis could be obtained for this compound.

2a,8,9,12,13,14,15,17,18,25,26,29,30,31,32,34,35,38b-Octadecahydro-2a,38b-diphenyl-13,30-bis(α-chloroacetyl)-1*H*,4*H*-6,37:20,23-dietheno-2,22:3,21-dimethano-5*H*,11*H*,28*H*,38*H*-7,10,16,19,24,27,33,36-octaoxa-2,3,4a,13,30,38a-hexaazacyclopenta[*cd*]cyclotetratriacont[*g*]azulene-1,4-dione (3): A solution of α-chloroacetyl chloride (100 mg, 0.90 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of **1a** (180 mg, 0.210 mmol) and TEA (40 μL) in CH_2Cl_2 (15 mL). The reaction mixture was stirred overnight at ambient temperature. After the addition of further CH_2Cl_2 (50 mL), the mixture was washed twice with saturated aqueous $NaHCO_3$ solution and once with water, and dried over $MgSO_4$. Purification by column chromatography (silica, $CHCl_3$/MeOH, 99:1, *v*/*v*) yielded 128 mg (60%) of **3** as a white powder; m.p. 271 °C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.59−4.41 (m, 32 H, CH_2O, CH_2N, NC*H*HAr, CH_2Cl), 5.68, 5.70, 5.74 (3 d, *J* = 16.35, 17.22, 16.47 Hz, 4 H, NCH*H*Ar), 6.66 (m, 4 H, ArH), 7.09 (m, 10 H, PhH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.07 (NCH_2Ar), 45.73, 45.79, 49.71, 49.82 (CH_2Cl), 68.39, 68.62, 68.97, 69.36, 69.44, 69.73, 70.05 (CH_2O, N$CH_2$$CH_2$O), 85.08 (NCN), 110.37, 110.49, 111.18, 111.28 (ArC), 127.78, 128.08, 128.27, 128.41, 128.53, 128.62 (PhC, ArC), 133.64 (PhC), 149.43, 149.61, 150.23, 150.59 (ArC), 157.94 [NC(O)N], 167.59 [*C*(O)CH_2]. − FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3068, 3041 (ArH), 2923, 2865 (CH_2), 1711 (C=O, urea), 1653 (C=O, amide), 1459, 1426 (CH_2), 1088, 1075 (COC), 768, 695 (Ar). − FAB-MS; *m*/*z*: 1029 [M + 1]$^+$. − $C_{52}H_{58}Cl_2N_6O_{12}$·$CH_3OH$ (1062.0): calcd. C 59.94, H 5.88, N 7.91; found C 59.80, H 5.99, N 7.90.

2a,8,9,12,13,14,15,17,18,25,26,29,30,31,32,34,35,38b-Octadecahydro-2a,38b-diphenyl-13,30-bis(α-thioacetyl-acetyl)-1*H*,4*H*-6,37:20,23-dietheno-2,22:3,21-dimethano-5*H*,11*H*,28*H*,38*H*-7,10,16,19,24,27,33,36-octaoxa-2,3,4a,13,30,38a-hexaazacyclopenta[*cd*]cyclotetratriacont[*g*]azulene-1,4-dione (4): Under N_2 atmosphere, a solution of potassium thiocarboxylate (114 mg, 2.50 mmol) in DMF (5 mL) was added dropwise to a solution of **3** (100 mg, 0.094 mmol) in DMF (10 mL) and the resulting mixture was stirred overnight under the exclusion of light. It was subsequently filtered and the filtrate was concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (50 mL) and this solution was washed twice with saturated aqueous $NaHCO_3$ solution and dried over $MgSO_4$. Purification by column chromatography (silica, $CHCl_3$/MeOH, 99:1, *v*/*v*) yielded 100 mg (96%) of **4** as a white powder; m.p. 259 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 [s, 6 H, C(O)CH_3], 3.69−4.16 (m, 32 H, CH_2O, CH_2N, NC*H*HAr, CH_2S), 5.71, 5.74 (2 d, *J* = 16.23, 16.29 Hz, 4 H, NCH*H*Ar), 6.67 (m, 4 H, ArH), 7.11 (m, 10 H, PhH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.90 (CH_3), 37.62 (NCH_2Ar), 46.69, 50.57 (CH_2S), 69.19, 69.34, 69.79, 70.01, 70.12, 70.31, 70.45, 70.66 (CH_2O, N$CH_2$$CH_2$O), 85.72 (NCN), 110.43, 112.22 (ArC), 128.62, 128.87, 128.97, 129.03, 129.18, 129.31 (PhC, ArC), 133.64 (PhC), 150.35, 150.41, 150.96, 151.05 (ArC), 158.08 [NC(O)N], 168.85 [*C*(O)CH_2], 195.87 [SC(O)]. − FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3062 (ArH), 2924, 2866 (CH_2), 1724 (C=O, thio ester), 1711 (C=O, urea), 1689 (C=O, amide), 1458 (CH_2), 1129, 1092 (COC), 770 (CCl). − FAB-MS; *m*/*z*: 1109 [M + 1]$^+$. − $C_{56}H_{64}N_6O_{14}S_2$ (1109.2): calcd. C 60.64, H 5.82, N 7.58, S 5.78; found C 60.27, H 5.70, N 7.41, S 5.80.

2a,8,9,12,13,14,15,17,18,25,26,29,30,31,32,34,35,38b-Octadecahydro-2a,38b-diphenyl-13,30-bis(α-thioacetyl)-1*H*,4*H*-6,37:20,23-dietheno-2,22:3,21-dimethano-5*H*,11*H*,28*H*,38*H*-7,10,16,19,24,27,33,36-octaoxa-2,3,4a,13,30,38a-hexaazacyclopenta[*cd*]cyclotetratriacont[*g*]azulene-1,4-dione (L^{Ac}2H): This compound was synthesized as described for L^{Xyl}2H. As starting material, **4** (100 mg, 0.090 mmol) was used. This was suspended in MeOH (5 mL) containing 3% HCl. CH_2Cl_2 was added to this suspension until a clear solution was obtained. After workup, 92 mg (100%) of L^{Ac}2H was obtained as a white powder; m.p. 275 °C (dec.). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.20 (dt, *J* = 2, 6 Hz, 2 H, SH), 3.51−4.25 (m, 32 H, CH_2O, CH_2N, NC*H*HAr, CH_2S), 5.69, 5.70, 5.75 (3 d, *J* = 16.24, 16.16, 16.21 Hz, 4 H, NCH*H*Ar), 6.66 (m, 4 H, ArH), 7.10 (m, 10 H, PhH). − FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3064, 3025 (ArH), 2920, 2847 (CH_2), 2536 (SH), 1711 (C=O, urea), 1642 (C=O, amide), 1460, 1426 (CH_2), 1129, 1087 (COC), 770, 703 (Ar). − FAB-MS; *m*/*z*: 1025 [M + 1]$^+$. − $C_{52}H_{60}O_{12}N_6S_2$ (1025.2): calcd. C 60.92, H 5.90, N 8.20, S 6.26; found C 61.05, H 5.87, N 8.13, S 6.23.

$(PPh_4)_2[Fe_4S_4(L^{Xyl})_2]$ (Cluster A): A suspension of $(PPh_4)_2[Fe_4S_4(S$*t*$Bu)_4]$ (55.2 mg, 0.040 mmol) in DMF (5−10 mL)

was added dropwise to a stirred solution of dithiol $\mathbf{L^{Xyl}}2H$ (93 mg, 0.081 mmol) in DMF (30 mL). The resulting mixture was stirred in vacuo for ca. 30 min. and then under N_2 atmosphere overnight. It was then filtered through a glass sinter disc and concentrated in vacuo. A large volume of Et_2O was carefully added to precipitate the product. After storage overnight at −20 °C, the product, a black solid, was isolated by decantation of the supernatant and drying in vacuo. The yield was not determined. − ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 2.77 (br. m, 16 H, NCH_2CH$_2$O), 3.42−4.12 (m, 64 H, CH$_2$O, NC*H*HAr, NCH_2ArCH$_2$), 5.50 (br. m, 8 H, NCH*H*Ar), 6.50 (br. s, 8 H, ArH), 7.14 (br. s, 20 H, PhH), 7.80 (m, 40 H, PPh_4), 14.30 (br. s, 8 H, CH_2S). − UV/Vis (DMF): λ_{max} (ε/ $M^{-1}\cdot cm^{-1}$) = 295 (33,600), 423 (11,100), 620 nm (sh, 1800). For further characterization, see text.

$(PPh_4)_2[Fe_4S_4(L^{Ac})_2]$ (Cluster B): To a suspension of dithiol $\mathbf{L^{Ac}}2H$ (100 mg, 0.097 mmol) in DMF (25 mL) was added dropwise a suspension of $(PPh_4)_2[Fe_4S_4(S\mathit{t}Bu)_4]$ (51 mg, 0.037 mmol) in DMF (10 mL). The resulting mixture was stirred under dynamic vacuum for 30 min. and then overnight under N_2 atmosphere. After filtration, the filtrate was concentrated in vacuo to a volume of a few mL. A large volume of Et_2O was then carefully added and the reaction flask was placed in a refrigerator at −20 °C overnight. This resulted in the precipitation of a black powder. After a second precipitation with Et_2O, the product was dried in vacuo. The yield was not determined. − ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 3.42−3.96 (m, 60 H, CH$_2$O, CH$_2$N), 3.66 (8 H, NC*H*HAr), 5.51 (br. m, *J* = 13.3 Hz, 8 H, NCH*H*Ar), 6.80 (br. m, 8 H, ArH), 7.08 (m, 20 H, PhH), 7.78 (m, 40 H, PPh_4), 14.09 (br. s, 8 H, CH_2S). − UV/Vis (DMF): λ_{max} (ε/ $M^{-1}\cdot cm^{-1}$) = 295 (40,200), 340 (sh, 17,400), 415 (13,400), 622 nm (sh, 3400). For further characterization, see text.

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