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Molecular Recognition of Aromatic Nitro Compounds at Cyclodextrin Dithiocarbamate-modified Electrodes

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Silver electrodes were modified by the adsorption of α-, β-, and γ-cyclodextrin dithiocarbamates (2α–γ) and characterized by reductive desorption experiments. Their molecular recognition properties were studied by cyclic voltammetry using three families of positional isomers of aromatic nitro compounds. Electrodes modified with 2α and 2β were selective for *meta* and *para* isomers while 2γ showed little selectivity. These observations are explained in terms of cavity sizes and guest structure. Computational studies suggest that the main reason for the observed selectivity is the different position of the NO_2 group in *ortho* and *para* isomers with respect to the CD cavity.

Keywords: Cyclodextrin; Dithiocarbamate; Self-assembled monolayer; Molecular recognition; Nitro compounds

INTRODUCTION

Cyclodextrins (CD) are a family of cyclic oligomers composed of α-(1 → 4)-linked D-glucopyranose units in the $^4C_1$ chair conformation. As a consequence of this peculiar structure, the molecule features a central cavity of hydrophobic nature. The most common CDs have 6, 7, and 8 glucose units and are named α-, β- and γ-CD, respectively. The inner diameter of the cavity in unmodified cyclodextrins varies from 4.7 to 8.3 Å and is about 8 Å in depth. These dimensions allow the inclusion of several types of guest molecule of appropriate size [1,2].

Molecular recognition systems based on cyclodextrin derivatives have been extensively studied and applied in fields such as drug delivery systems, enzyme modeling, sensing devices, etc. [3]. In particular, self-assembled monolayers (SAM) of thiolated cyclodextrin derivatives on gold surfaces have attracted great interest due to their potential application as selective electrodes [4–10]. The adsorption of cyclodextrin receptor surfaces provides the electrode with molecular recognition properties in which electroactive or non-electroactive probes and other interfacial phenomena can be studied. As far as we know, only the thiolate group has been used in previous works as the attachment point. Thus, little is known about the SAM-forming properties of other families of sulfur-containing derivatives.

In a previous communication [11], we reported that a β-cyclodextrin dithiocarbamate forms a SAM on silver electrodes with the ability to discriminate between isomeric nitrobenzoate ions. In the present work, we describe the synthesis and molecular recognition properties of a series of dithiocarbamate-containing α-, β- and γ-cyclodextrins adsorbed onto silver surfaces. These hosts were also designed to study the influence of the cavity size on the molecular recognition properties. As probes, several families of isomeric aromatic nitro compounds were studied. Cyclic voltammetry and computational studies were used to account for the obtained results.

RESULTS AND DISCUSSION

Syntheses and Characterization of the Cyclodextrin Hosts

The cyclodextrin receptors were prepared by reaction of the readily available per-6-amino-6-deoxycyclodextrins

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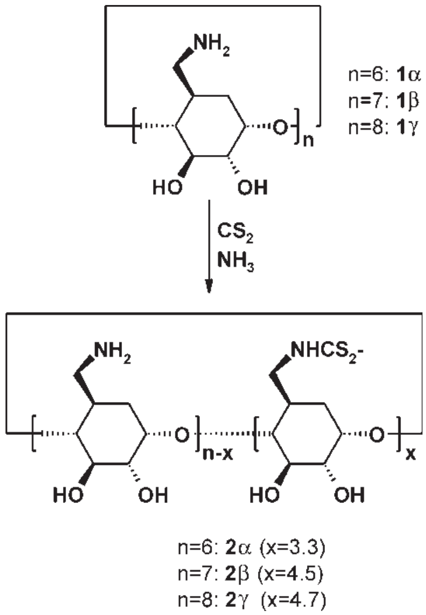

FIGURE 1 Synthesis of the cyclodextrin hosts.

TABLE I Desorption and coverage characteristics of the studied electrodes

Electrode	$E_{desorption}$ (V)*	Γ (pmol/cm^2)†	Coverage ratio (%)†
Ag/**2**α	− 0.72	50	72
Ag/**2**β	− 0.69	44	63
Ag/**2**γ	− 0.67	42	60

* Recorded in 0.5 M KOH at 50 mV/cm. † Assuming 3, 4 and 5 Ag–S bonds for **2**α, **2**β and **2**γ, respectively. Error < 8%.

1α–γ [12] with stoichiometric amounts of CS$_2$ in ammonia solution (Fig. 1). This method is essentially similar to that reported previously for the synthesis of mono-substituted derivatives [13].

The ^{1}H NMR spectra of these materials in D$_2$O show a singlet at ~5.1 ppm (anomeric protons) and a multiplet centered at 3.5 ppm corresponding to the other skeletal protons. The ^{13}C NMR spectra show the characteristic signal of the NCSS group as a broad signal centered at ~213 ppm. The signals in both spectra are substantially broadened suggesting that **2**α–γ are, in fact, a mixture of materials having different degrees of substitution, that is, the substitution of amino groups is incomplete. Unfortunately, we were unable to obtain FAB, ES or MALDI-TOF mass spectra of these products even under a variety of conditions. The degree of substitution of dithiocarbamate groups (x) was then estimated from the NOE-suppressed proton-decoupled ^{13}C spectra of **2**α–γ. Integration of the NCSS signal (~213 ppm) relative to that of the anomeric carbon (~104 ppm) gave 55%, 64% and 59% substitution and, therefore, $x = 3.3$, 4.5 and 4.7 in the formula of **2**α, **2**β and **2**γ, respectively (Fig. 1). This fact suggests that the primary rim of cyclodextrins is not capable of accommodating 6, 7 or 8 dithiocarbamate groups, respectively, presumably for steric reasons. Further attempts to increase the degree of substitution by increasing the amount of CS$_2$ were unsuccessful.

Monolayer Characterization

Monolayer formation was carried out by immersing the silver electrode in a DMSO solution of **2**α–γ overnight. By monitoring the time-dependent decrease of redox peaks of a 1 mM solution of Ru(NH$_3$)$_6^{3+}$ we were able to follow the adsorption kinetics of these products. It was found that the adsorption process is very fast in the first minutes after immersion but is complete only after 10 h.

Reductive desorption experiments were carried out to confirm the chemisorption of **2**α–γ onto the electrode surface (Table I). The cyclic voltammogram of **2**β recorded in 0.5 M KOH shows an irreversible reductive peak at −0.69 V vs. Ag/AgCl, which can be assigned to the reductive desorption of **2**β (Fig. 2). Two small anodic signals are also visible at −0.58 V and −0.62 V. These signals do not appear when the potential is scanned from 0 to −0.6 V, thus we assign them to the partial readsorption of desorbed **2**β. Integration of the cathodic peak at −0.69 V and normalization to the electrode surface gives 63% surface coverage, taking into account the formation of 4 Ag–S bonds and a maximum surface concentration $\Gamma_{max} = 70$ pmol/cm^2. These coverage values are similar to those reported for a per-6-thio-β-cyclodextrin monolayer [4] although care should be taken when comparing these values due to the polydispersion of the sample. **2**α showed the highest surface coverage suggesting that this host is better packed at the electrode surface due to its smaller size.

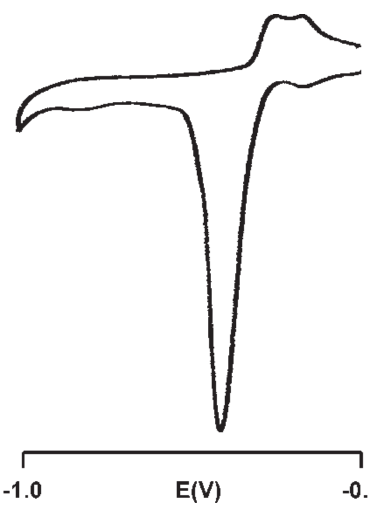

FIGURE 2 Cyclic voltammogram for the reductive desorption of 2β in 0.5 M KOH at 50 mV/s.

TABLE II Potentials (V) of the reduction of the NO_2 group of the studied nitro compounds[*]

	Nitrobenzoate			Nitrophenol			Nitrobenzyl alcohol		
Electrode	*ortho*	*meta*	*para*	*ortho*	*meta*	*para*	*ortho*	*meta*	*para*
Bare Ag	−0.48	−0.30	−0.44	−0.26	−0.56	−0.26	−0.36	−0.35	−0.34
Ag/**2**α	–[†]	−0.43	−0.48	–[†]	−0.58	−0.32	–[†]	−0.40	−0.39
Ag/**2**β	–[†]	−0.34	−0.42	–[†]	−0.57	−0.28	–[†]	−0.39	−0.36
Ag/**2**γ	−0.51	−0.32	−0.40	−0.30	−0.56	−0.26	−0.39	−0.38	−0.30

[*] Recorded at 100 mV/s in 10 mM probe solutions using 0.2 M Na_2SO_4 as the supporting electrolyte. [†] No signal is observed.

$Fe(CN)_6^{3-}$ was used to check monolayer formation and permeation. At the bare silver electrode, this probe shows a signal at $E_{1/2} = 0.45$ V vs. Ag/AgCl with a peak separation $\Delta E_{ac} = 60$ mV. ΔE_{ac} increases to 120 mV for the Ag/**2**β electrode with a +0.04 V shift in $E_{1/2}$. These observations can be explained in terms of the decrease in electron transfer rate caused by the barrier of chemisorbed **2**β.

Since for molecular recognition studies it is important that the electroactive molecules interact only with the electrode through the CD cavities, the uncovered surface has to be sealed with an appropriate agent. In the present work we used sodium morpholyldithiocarbamate (MorDTC) for this purpose. Sealing was confirmed by desorption experiments and also using $Fe(CN)_6^{3-}$. For Ag/**2**β this probe showed values of $E_{1/2} = 0.52$ V and $\Delta E_{ac} = 140$ mV with a 15% reduction of the peak currents. A similar trend was observed for the Ag/**2**α and Ag/**2**γ electrodes. When adamantanol was added to the solution of $Fe(CN)_6^{3-}$ the signals disappeared. This is due to the competition of these guests for the CD cavities, indicating that MorDTC completely sealed the remaining area between the adsorbed CDs on the electrode surface.

Molecular Recognition Properties

The molecular recognition properties of the CD-modified electrodes were studied using several families of aromatic nitro compounds. Aromatic nitro compounds undergo a four-electron reduction to hydroxylamines at negative potentials in neutral or acid media [14] and also form inclusion complexes with CDs [15,16]. In our study, we selected the three positional isomers of nitrobenzoate, nitrophenol and nitrobenzyl alcohol as probes to study the molecular recognition ability of the CD-modified electrodes. The results are summarized in Table II and a selection of representative voltammetric responses is depicted in Fig. 3.

One characteristic that arises from the analysis of the cyclic voltammograms is a decrease in signal intensity of 20–30% with respect to the bare electrode. This is expected as the monolayer of chemisorbed receptors and sealing agent significantly reduces

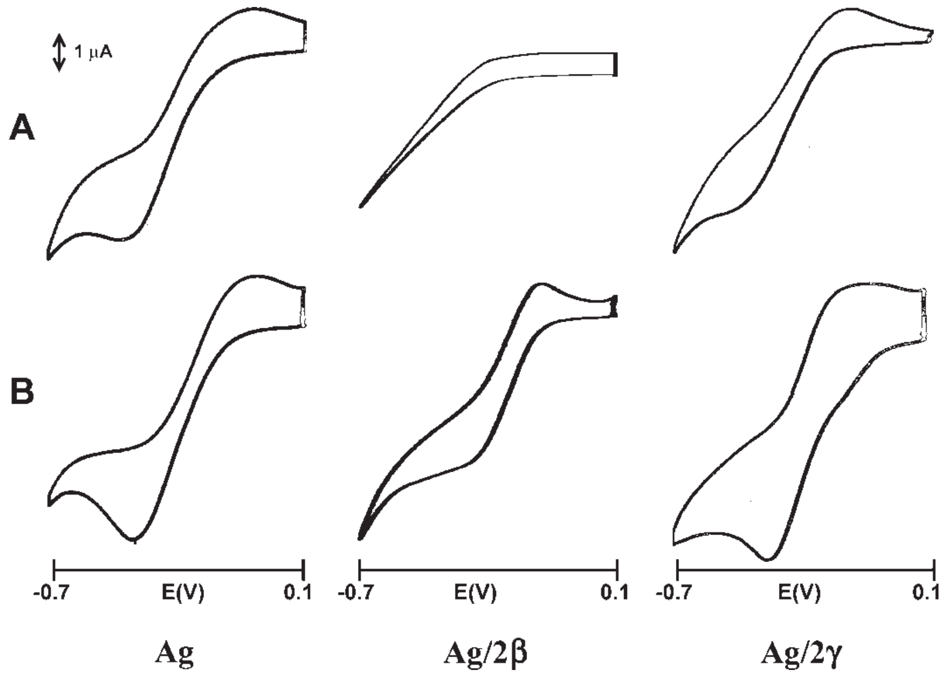

FIGURE 3 Cyclic voltammetric responses of 10 mM solutions of *ortho*-nitrobenzoate (A) and *meta*-nitrobenzoate (B) recorded at bare Ag (left), Ag/**2**β (center) and Ag/**2**γ (right) electrodes. Supporting electrolyte: 0.2 M Na_2SO_4. Scan rate: 100 mV/s.

the working area of the electrode, decreasing the signal intensity. Experiments with several *meta* and *para* compounds in the presence of adamantanol showed a large decrease (~70%) in signal intensity. This observation suggests the competitive complexation of adamantanol as a guest and, therefore, that the electroactive probe actually reacts with the electrode through the CD cavities.

Remarkably, the *ortho* isomer of the three probes does not give any signal at Ag/**2**α and Ag/**2**β electrodes, at least at accessible potentials. We studied this process over a wide range of concentrations (1 μM–10 mM) and the absence of signal was found even at 10 mM probe concentration. In the case of the other two isomers no such high concentrations were needed to observe a signal. For instance, saturation behavior of the reduction peak intensity of *meta*- and *para*-nitrophenol at the Ag/**2**β electrode was found for probe concentrations above 0.25 mM and 0.46 mM, respectively. This clearly indicates interfacial complexation of the probe to the immobilized CD hosts. Langmuir treatment of the bulk concentration vs. surface coverage data for both systems gave $K_{as} = 180 \pm 20\,M^{-1}$ and $140 \pm 20\,M^{-1}$ for *meta*- and *para*-nitrophenol, respectively, values similar to those reported for the complexation of these guests with native β-CD [15,16]. Maximum surface coverages obtained from these data were about 20% lower than those reported for the immobilized CD host, suggesting that not all the CD molecules are capable hosting the probe at the monolayer level as a result of a relatively low association constant. However, at higher concentrations (>1 mM) where diffusion dominates the voltammetric response, the signal intensity increases steadily with the bulk concentration of the probe.

The above observations and the lack of response for the *ortho* isomer suggest that the Ag electrodes modified with monolayers of **2**α and **2**β are selective for *meta* and *para* isomers. In the *ortho* isomer, both functional groups are next to each other provoking a steric effect great enough to avoid the inclusion and orientation of the NO_2 group towards the silver surface. This geometric feature, combined with the relatively small size of **2**α and **2**β, is expected to hinder the reduction of the nitro group to a point where no signal is observed up to −0.7 V. At the Ag/**2**γ electrode this isomer does give a signal but shifted to more negative potentials. This is expected considering that the larger cavity of **2**γ is capable of including *ortho* isomers.

In the case of *meta* and *para* isomers, the general trend is also a negative shift in the reduction peak, showing the highest shift (−0.13 V) for *m*-nitrobenzoate at the Ag/**2**α electrode. For these isomers, the peak potentials are displaced to more negative values in the order **2**α > **2**β > **2**γ suggesting a direct influence of the cavity size on the electroactive response. Both *meta* and *para* isomers can be included in the receptor cavity in such a way that the nitro group is susceptible to interaction with the silver surface. In general, nitrophenols gave the lowest peak shifts while nitrobenzoates gave the highest. This can be rationalized in terms of the lesser bulkiness of hydroxy groups with respect to carboxylate substituents.

Computational Study

Computational chemistry is gaining increased value as a tool for the prediction and elucidation of molecular recognition events in CDs [17,18]. To complement the results obtained with the voltammetric experiments, we performed a series of semiempirical quantum mechanical calculations using the PM3 Hamiltonian [19–21]. As a host we selected tetrakis-$6^A,6^B,6^D,6^F$-β-cyclodextrin

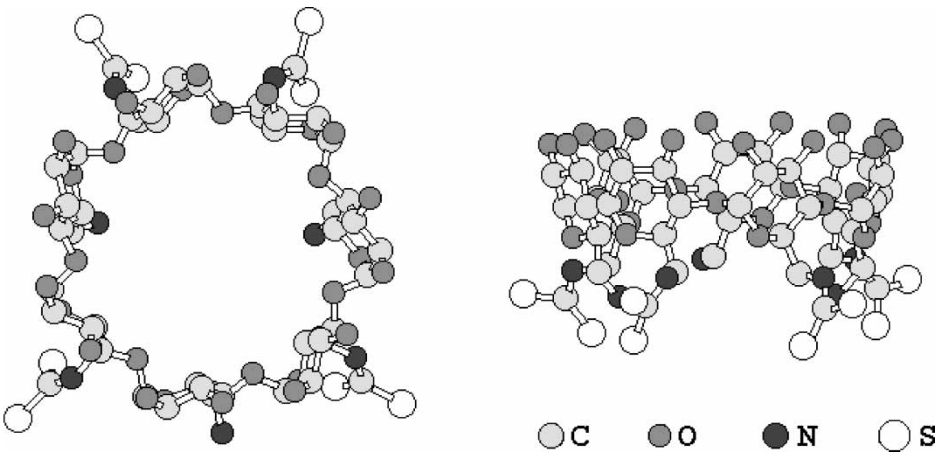

FIGURE 4 Optimized geometry obtained from PM3 calculations for tetrakis-$6^A,6^B,6^D,6^F$-β-cyclodextrin dithiocarbamate. Hydrogen atoms are omitted for clarity. Left: top view from the secondary hydroxy side. Right: lateral view.

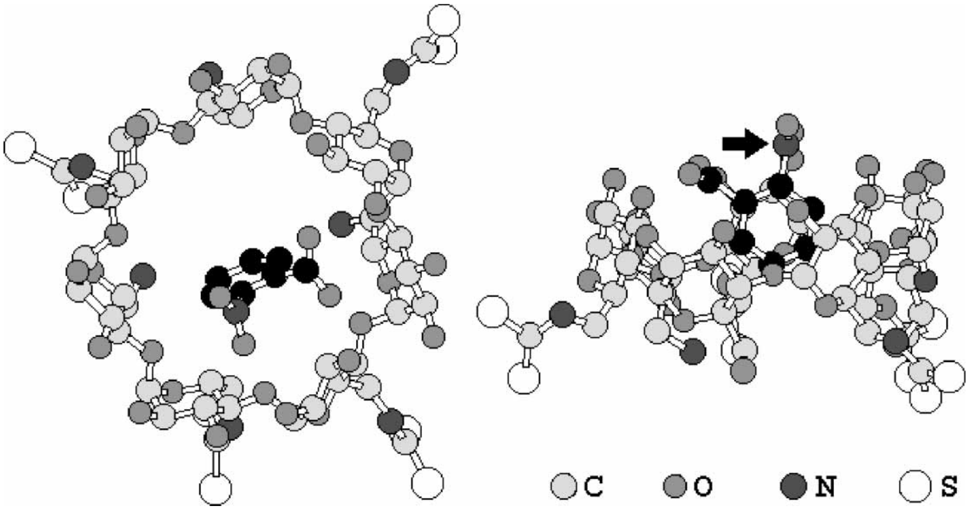

FIGURE 5 Optimised geometry obtained from PM3 calculations for the inclusion complex of *ortho*-nitrobenzoate with tetrakis-$6^A,6^B,6^D,6^F$-β-cyclodextrin dithiocarbamate. The carbon atoms of the guest are highlighted in black. Hydrogen atoms are omitted for clarity. Left: top view from the secondary hydroxy side. Right: lateral view showing the NO_2 group pointing outside the cavity (indicated with an arrow).

dithiocarbamate,† taking into account that the degree of substitution in **2**β is close to 4. The optimized geometry of this host (Fig. 4) suggests that the four NCSS groups lie in an almost regular plane with a circular cavity of 7.5 Å inner diameter and 8.2 Å depth.

Figures 5 and 6 show, respectively, the PM3 optimized geometries of the inclusion complexes of *ortho*- and *para*-nitrobenzoate with the tetrasubstituted host. As can be seen from Fig. 5, the *ortho*-nitrobenzoate guest is only partially included in the β-CD cavity through the aromatic ring, with the substituents pointing outwards. The nitrogen atom of the NO_2 group is separated 8.5 Å with respect to the plane formed by the NCSS groups and there is an H-bond between the carboxylate group and one secondary hydroxy group of the β-CD rim. Although we did not perform calculations with an α-CD derivative, it is expected that the *ortho*-nitrobenzoate guest is less included than in a β-CD cavity due to the smaller size of α-CD. In the case of γ-CD hosts, MM2 calculations (data not shown) suggest that this guest can be included in the cavity in several ways with minimal energy differences. In one of them the guest molecule lies with the $N_{nitro}-C_{carboxylic}$ axis almost parallel to the γ-CD pseudo-C_8 axis, thus making possible the interaction with the electrode surface when the NO_2 group points toward the primary side of the γ-CD.

In contrast, *para*-nitrobenzoate fits perfectly into the β-CD host (Fig. 6) with the NO_2 deeply included in the cavity and separated by only 2.5 Å from the plane of NCSS groups. As in the *ortho* isomer, the structure is stabilized by H-bonding involving the carboxylate group, which makes the guest appear twisted about 20° from an imaginary pseudo-C_7 axis. Of course, the calculation also predicts an inverted orientation of the guest but this geometry is 15 kcal less stable.

In view of these results, the opposite electroactive responses of *ortho*- and *para*-nitrobenzoate could be explained considering the different geometries arising from their inclusion in the CD cavity. In the first case, the NO_2 group cannot penetrate into the cavity, preventing, or at least retarding to a large extent, the electron transfer process.

CONCLUSIONS

The results presented in this paper suggest that the molecular recognition properties of CD-modified electrodes toward isomeric probes can be tuned by an appropriate selection of receptor size and guest geometry. Recognition can be established by the different degrees of signal shift or disappearance associated with the inclusion process. It seems plausible that these types of electrode are capable of recognizing the positional isomers of other electroactive aromatic and cyclic compounds.

EXPERIMENTAL

Synthesis and Characterization

1 mmol of **1**α, **1**β or **1**γ [12] was suspended in a 1:1:1 (v/v) solution of 25% aqueous NH_3, water and

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†This nomenclature is interpreted as follows: the cyclodextrin core is viewed from the primary side, then each glucose unit is labeled clockwise A, B, C, etc. Thus, $6^A,6^B,6^D,6^F$ means that the four dithiocarbamate groups are located in the 6 position of units A, B, D and F, respectively.

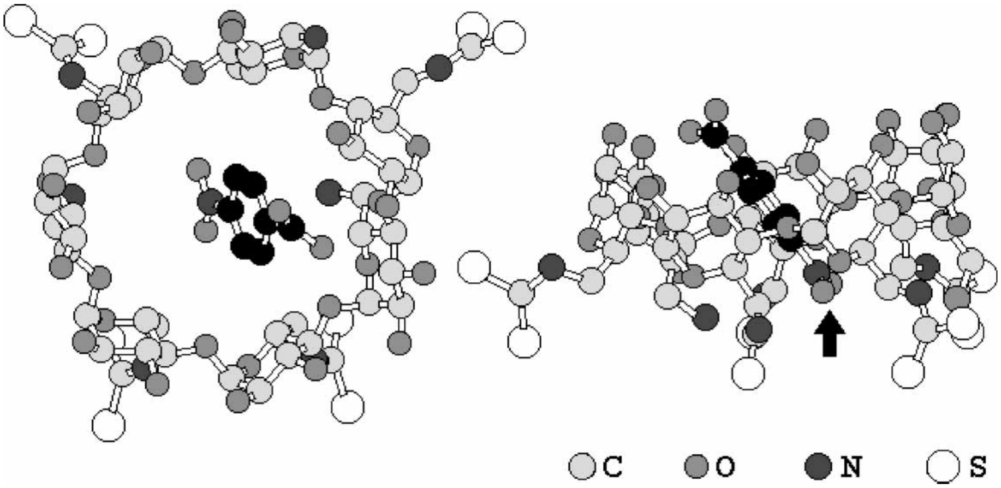

FIGURE 6 Optimised geometry obtained from PM3 calculations for the inclusion complex of *para*-nitrobenzoate with tetrakis-$6^A,6^B,6^D,6^F$-β-cyclodextrin dithiocarbamate. The carbon atoms of the guest are highlighted in black. Hydrogen atoms are omitted for clarity. Left: top view from the secondary hydroxy side. Right: lateral view showing the NO_2 group deeply embedded in the cavity (indicated with an arrow).

ethanol (60 ml) and 6, 7 or 8 equivalents, respectively, of freshly distilled CS_2 were added. The reaction mixture was vigorously stirred for 6 h at room temperature (the solid dissolves slowly), then precipitated with acetone (250 ml). The product was filtered off, washed several times with acetone and dried under vacuum to give **2**α, **2**β or **2**γ as white powders in 70–75% yield.

The degree of substitution of dithiocarbamate groups on the primary rim (x) was determined from the integrated NOE-suppressed proton-decoupled ^{13}C NMR spectra of **2**α–γ in DMSO-d_6. Thus, x was calculated as the ratio between the integration of the NCSS signal (~212 ppm) and the C_1 signal (~104 ppm). Typical conditions for NMR experiments were: sample concentration: 30 mg/0.5 ml; spectral width: 20,000 Hz, 32 K points; pulse width: 4 μs; relaxation delay: 10 s; number of scans: 4800.

2α: ^{13}C NMR: δ (ppm) 212.6 (CSS), 101.5 (C-1), 84.0 (C-4), 70–72 (C-2, C-3, C-5), 56.7 (C-6′), 52.4 (C-6). UV: $\lambda_{\max}$ (ε), 249 nm (45,000) (ππ* CSS), 289 nm (49,000) (ππ* NCS).

2β: ^{13}C NMR: δ (ppm) 214.5 (CSS), 102.1 (C-1), 83.4 (C-4), 70–72 (C-2, C-3, C-5), 56.5 (C-6′), 52.5 (C-6). UV: $\lambda_{\max}$ (ε), 248 nm (43,000) (ππ* CSS), 287 nm (47, 200) (ππ* NCS).

2γ: ^{13}C NMR: δ (ppm) 213.7 (CSS), 102.2 (C-1), 84.1 (C-4), 70–72 (C-2, C-3, C-5), 57.1 (C-6′), 53.0 (C-6). UV: $\lambda_{\max}$ (ϵ), 248 nm (40,800) (ππ* CSS), 288 nm (45,100) (ππ* NCS).

Electrochemistry

Cyclic voltammograms were recorded on a Yanaco P-900 cyclic polarograph coupled to a Graphtec WX1000 X–Y recorder using a standard three cell holder [counter electrode: Pt flag, reference: Ag/AgCl(sat)]. All solutions were deoxygenated with argon before the measurements were taken. The supporting electrolyte was 0.2 M Na_2SO_4 and the scan rate was 100 mV/s unless otherwise stated.

The modified Ag electrodes were prepared as follows. Home-built silver beads ($A = 0.10–0.12\ cm^2$) were prepared by annealing the tip of a 1 mm diameter silver wire (99.99% purity, Aldrich) previously cleaned with dilute nitric acid. The beads were cooled under an argon stream, then cleaned again with dilute nitric acid and washed with water and ethanol. Geometric areas were calculated using $Ru(NH_3)_6^{3+}$ as previously described [4] and were corrected for roughness, which was estimated to be 1.2.

The silver beads were immersed in a 0.01 M DMSO solution of **2**α–γ overnight, followed by immersion in a 0.01 M DMSO solution of MorDTC for 8 h. The electrodes were rinsed with DMSO, EtOH and doubly distilled water and voltammetrically tested in 0.1 M KH_2PO_4 and 0.2 M Na_2SO_4, giving a flat background response between 0 V and −0.6 V.

Computational Study

Quantum mechanical calculations were performed with the PM3 Hamiltonian [19–21] contained in MOPAC 6.0 [22] using a Pentium IV Personal Computer. The starting host geometry was the crystal structure of β-CD [23,24], in which the seven primary hydroxy groups were replaced by amino groups. This structure was first minimized at the MM2 level using HyperChem™ software [25], the four CSS groups were added and the geometry was finally optimized at the PM3 level. Previous calculations on the five possible positional isomers of a tetrasubstituted β-CD dithiocarbamate ($6^A,6^B,6^C,6^D$-, $6^A,6^B,6^C,6^E$-, $6^A,6^B,6^C,6^F$-, $6^A,6^B,6^D,6^E$- and $6^A,6^B,6^D,6^F$-) suggested that the last-mentioned host is the most stable because the electrostatic repulsion between the four negatively charged groups is minimal. Therefore, this isomer was selected for the subsequent studies.

For the calculations of the inclusion complexes, the optimized guests, *ortho*- and *para*-nitrobenzoate, were located in the interior of the cavity and the resulting structure was then minimized at the PM3 level. The host geometry was not fixed. The NCSS groups were protonated to mimic the adsorption onto the metal surface and also to avoid any electrostatic contribution coming from these groups. All calculations achieved a self-consistent field and were complete when the gradient was less than $0.1\,\mathrm{kJ}\,\text{Å}^{-1}\,\mathrm{mol}^{-1}$. Computer graphics were generated with ORTEP-3 for Windows, version 1.075 [26].

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