ORIGINAL ARTICLE

Determination of the surface acidity of a free-base corrole in a self-assembled monolayer

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Abstract Mixed self-assembled monolayers (SAMs) containing a corrole moiety have been prepared to examine their electrochemical properties and surface acidity, with the eventual goal of biosensor development. Mixed SAMs consisting of 6-mercapto-hexanol (6-MHO) and 8-amino-1-octanethiol (8-AOT) in varying ratios were modified with a free-base corrole and characterized via Osteryoung square-wave voltammetry and contact angle measurements. The surface acidity of the free-base corrole was determined using an electrochemical titration method, with pK_a values established at 6.4 when using $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ as a redox probe and at 6.7 when using iodide, and assigned to the $CorH_4^+ \rightleftharpoons CorH_3 + H^+$ equilibrium.

Keywords Corrole · Mixed self-assembled monolayer · Osteryoung square-wave voltammetry · Surface pK_a · Electrochemical titration

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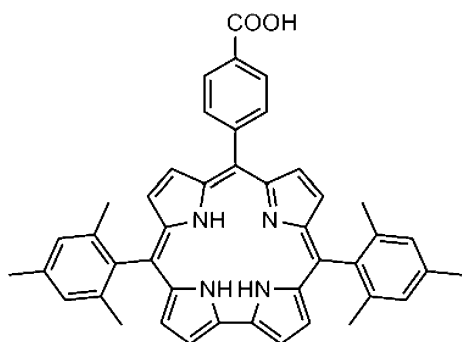Campus, Agoralaan Building D, 3590 Diepenbeek, Belgium

Introduction

Corroles are a class of compounds analogous to the ubiquitous porphyrins, but characterized by the lack of one *meso* carbon atom. This results in a contracted inner core and a more electron-rich π-system, leading to remarkable properties such as the ability to complex metal ions in unusual oxidation states [1]. Though originally marred by very low-yielding multi-step syntheses, research into corrole chemistry has increased dramatically since the discovery of high-yielding one-pot methods by Gross and Paolesse [2, 3] in 1999. With synthetic procedures continuously improving, opening up pathways to increasingly complex corroles, the number of possible applications of corroles, such as catalysts in oxidation [4], reduction [5–7] and group transfer reactions [8, 9], as sensors for organic and inorganic compounds [10–14], as dyes in solar cells [15], and even as pharmaceuticals [16], is ever-increasing, as recently reviewed by Aviv-Harel and Gross [17, 18]. However, unlike the large body of work on porphyrin-containing SAMs, corroles thus far have scarcely been employed in self-assembled monolayers (a search on Web of Science returns about 230 results for the query 'porphyrin self-assembled monolayer', yet only 1 result for 'corrole self-assembled monolayer').

For some time, our research group has been interested in the incorporation of macrocyclic pyrrole derivatives as transducers in SAM-based biosensors, such as dipyrromethenes and porphyrins [19–21]. More recently, our focus shifted towards the use of corroles in biosensors, resulting in the development of a method for the determination of dopamine in blood plasma using a corrole-containing SAM [22]. While our main efforts have been directed towards SAMs containing metalated corroles, a comparison with free-base corroles would help us explain corrole surface

Fig. 1 The free-base corrole

activity. In this paper, we set out to determine an important aspect of the free-base corrole used (Fig. 1)—its surface acidity and the influence on its electro-chemical behaviour.

In contrast to porphyrins, which have aqueous log K values of about 32 [23] and, for tetraarylporphyrins, undergo a single-step double protonation [24] to $PorH_4^{2+}$, corroles are truly amphoteric. This marked difference in acidity has been attributed to a massive release of steric strain upon going from a crowded, distorted inner core to a stable, porphyrin-like planar structure through the dissociation of a single proton [25]. On the other hand, steric strain is increased only slightly in the addition of an extra proton to a neutral corrole. Though several papers have been published on the subject of corrole acidity, due to the insolubility of corroles in aqueous media most of them used non-aqueous solvents such as benzonitrile or pyridine in the determination of the pK_a values [26, 27]. In one case, the pK_a values of the water soluble, highly acidic corrole 2,17-disulphonato-5,10,15-tris(penta-fluorophenyl)corrole were measured to be 2.5 (for $CorH_4^+ \rightleftharpoons CorH_3$) and 5.2 (for $CorH_3 \rightleftharpoons CorH_2^-$). However, the acidity of a free-base corrole incorporated into a SAM in aqueous media (or indeed, any media) has never been determined.

A number of different methods have been employed to determine the surface acidity of a SAM, including quartz-crystal microbalance [28], double-layer capacitance measurements [29], contact angle titration [30], atomic force microscopy, indirect laser-induced temperature jump studies (ILIT) [31], surface plasmon resonance spectroscopy [32] and electrochemical titrations [30, 33]. The pK_a values thus obtained, however, have a tendency of differing wildly between different methods, with divergences commonly being up to 3 or more pH units [33]. As such, the surface pK_a value of an acidic monolayer obtained using a particular method is not always comparable to the pK_a of the same compound in bulk solution. Moreover, depending on surface material and conditions used, the surface acidity can either increase or decrease [34, 35]. In the case of electrochemical titration techniques, the shifts in surface pK_a values observed with varying chain length or varying

surface density have been ascribed to changing electrostatic interactions between the end groups and are known to be dependent on the ionic strength of the electrolyte solution and the electric field present at the interface [36]. This latter phenomenon, known as electric field driven protonation/deprotonation, has also been applied in the determination of the surface pK_a of acidic mono-layers [37].

For our determination of the surface acidity, we opted for the electrochemical titration technique, as it is sensitive and convenient to use. Instead of cyclic voltammetry, however, we chose to use Osteryoung square-wave voltammetry (OSWV) due to its greater sensitivity.

Experimental

Materials

The free-base corrole (10-(4-carboxyphenyl)-5,15-bis(2,4,6-trimethylphenyl)corrole) was prepared at the Department of Chemistry of the K.U. Leuven, Belgium [38, 39].

Ethanol, methanol, chloroform, sulfuric acid, phosphoric acid, KH_2PO_4, K_2HPO_4, KOH and NaI were obtained from POCh (Gliwice, Poland). 1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC), 6-mercaptohexanol (6-MHO), (2-methyl-1-ferrocenylmethyl)trimethylammonium iodide (FcI), $K_3Fe(CN)_6$ and $K_2Fe(CN)_4$ were obtained from Fluka-Sigma-Aldrich (Poznan, Poland). 8-Aminooctanethiol (8-AOT) was obtained from Dojindo Laboratories (Japan). All chemicals were of analytical grade and were used as received.

All aqueous solutions were prepared using ultrapure water, purified with a Millipore system, with a resistivity of 18.2 MΩ cm, and deoxygenated using nitrogen gas for at least 10 min before any experiment. Electrochemical titrations were performed in 0.1 M potassium phosphate buffer solutions.

Equipment

All electrochemical measurements were performed on a potentiostat–galvanostat AutoLab (Eco Chemie, Utrecht, the Netherlands) using a three-electrode setup.

All potentials are reported versus an Ag/AgCl (3 M NaCl) reference electrode. A coiled platinum wire was used as the counter electrode. Working electrodes were polycrystalline gold disks (2 mm^2) coated in a Teflon jacket (BioAnalytical Systems (BAS), West Lafayette, IN). OSWV was performed in degassed 0.1 M KCl or 0.1 M potassium phosphate buffer solutions.

Contact angle measurements were performed on an OCA 15 + goniometer (Dataphysics Instruments, Filderstadt, Germany) using the sessile drop method.

Preparation of SAM

The working electrodes were first cleaned mechanically by rubbing them in 0.3 and 0.05 micron alumina slurries (Alpha and Gamma micropolish, Buehler, Lake Bluff, IL) on a polishing cloth for 5 min, followed by 30 s of sonication in MilliQ water. Next, electrochemical cleaning was performed by continuous cycling in 0.5 M KOH (−0.4 to −1.4 V) and 0.5 M H_2SO_4 (−0.3 to +1.5 V) solutions until the graphs remained stable.

The clean gold disk electrodes were then rinsed with water and ethanol and submerged for 30 min in an ethanolic solution of 6-MHO and 8-AOT in the appropriate concentrations. The electrode surfaces were rinsed with ethanol and water and allowed to stand in water for 4 h. Then, the electrodes were again rinsed with ethanol and submerged in a 1:1 mixture of methanol and chloroform containing 0.26 M EDC and 10^{-4} M of corrole. After 18 h, the gold surfaces were again rinsed with ethanol and water, and then left to stand in water overnight. The quality of the SAMs was checked by CV and OSWV in an aqueous 0.1 M KCl solution, giving highly reproducible results.

Gold plates for contact angle measurements were supplied by IMEC (Leuven, Belgium), and were cleaned by submersion in fresh 7:2 sulfuric acid : hydrogen peroxide solution (3 × 60 s), rinsed with MilliQ water and absolute ethanol, dried under N_2 followed by 20 min treatment in an ozone chamber. The gold plates were then immediately submerged into the modification solution for 30 min, rinsed with EtOH, conditioned in EtOH for 15 min, again rinsed with EtOH, dried under N_2 and immediately used for contact angle measurements. The corrole modification procedure was identical to the one used for the electrodes. All contact angle measurements were repeated at least twice on two different gold plates with a minimum of 3 drops per plate.

Results and discussion

Contact angle

The wettability of the modified surfaces was determined by contact angle measurements using the sessile drop method with water as the solvent. The contact angle values (Table 1)

were obtained as the average of at least 4 samples with at least 3 measurements per sample, and contact angles were measured immediately after droplet deposition. The lowest contact angles are seen with the mixed 6-MHO/8-AOT and with the neat 8-AOT monolayers, indicating very hydrophilic surfaces. The droplets spread very quickly on the surface and the measurement of the contact angle became impossible within seconds after deposition. Incorporation of corrole onto these surfaces increased the contact angle for both by about 15°, indicating that the average distance between the hydrophobic corrole moieties is leaving ample room for the solvent to penetrate to the amine layer and spread on the surface.

Electrochemistry

Osteryoung square-wave voltammetry (OSWV) experiments were performed in 0.1 M aqueous KCl and 0.1 M aqueous potassium phosphate buffers at pH 4.0, 6.0, 7.0 and 8.0, in the potential range of +0.6 to −0.6 V with a scan rate of 25 mV/s (ΔE_s = 1 mV, f = 25 Hz). Only one redox reaction can be observed (Fig. 2). This reaction, the reduction of oxidized corrole, occurs at +0.25 V in KCl and at about +0.40 V in phosphate buffer solution in the pH range of 4–7. No effect of the surface concentration of the Fb corrole on the peak potential could be observed in either KCl or phosphate buffer solution, though the potential is seen to move towards lower values when increasing the pH from 4 to 8 (from +0.40 to +0.34 V). This corresponds with a simultaneous decrease in current and correlates with a deprotonation reaction involving the free-base corrole (vide infra). A similar correlation has been observed with a free-base porphyrin SAM, with the authors concluding that the rate of electron transfer is increased when the porphyrin moieties are protonated [40].

That the peak current is generally the lowest (except at pH 8) when the surface concentration of corrole is highest, also corresponds to a similar observation by the same authors: a highly structured and densely packed porphyrin SAM was observed to decrease, to some degree, the rate of electron transfer between porphyrin core and gold electrode.

These results can be contrasted to the half-wave potentials ($E_{1/2}$) obtained for a comparable corrole, [(MePh)$_3$Cor]H$_3$, in the non-aqueous solvent benzo-nitrile [26]. In this case, a

Table 1 Water contact angle values for the SAMs (in degrees)

Modification	Contact angle	Modification	Contact angle
6-MHO:8-AOT 100:1	30.5 ± 1.9	8-AOT	28.2 ± 2.1
6-MHO:8-AOT 100:1 + FbCor	45.7 ± 2.6	8-AOT + FbCor	45.4 ± 3.8
Bare gold	9.9 ± 2.0		

Fig. 2 OSWV (vs. Ag/AgCl) spectra for Fb corrole SAM in **a** 0.1 M KCl, **b** 0.1 M phosphate buffer solution at pH 4, and **c** pH 8 at different surface concentrations; neat 8-AOT + FbCor (*solid lines*), 10% (*filled circles and dashed line*) and 1% (*filled circles*). **d** OSWV curves for 10% Fb corrole at pH 4 (*solid line*), 6 (*filled circles and dashed line*), 7 (*dashed line*) and 8 (*filled squares*)
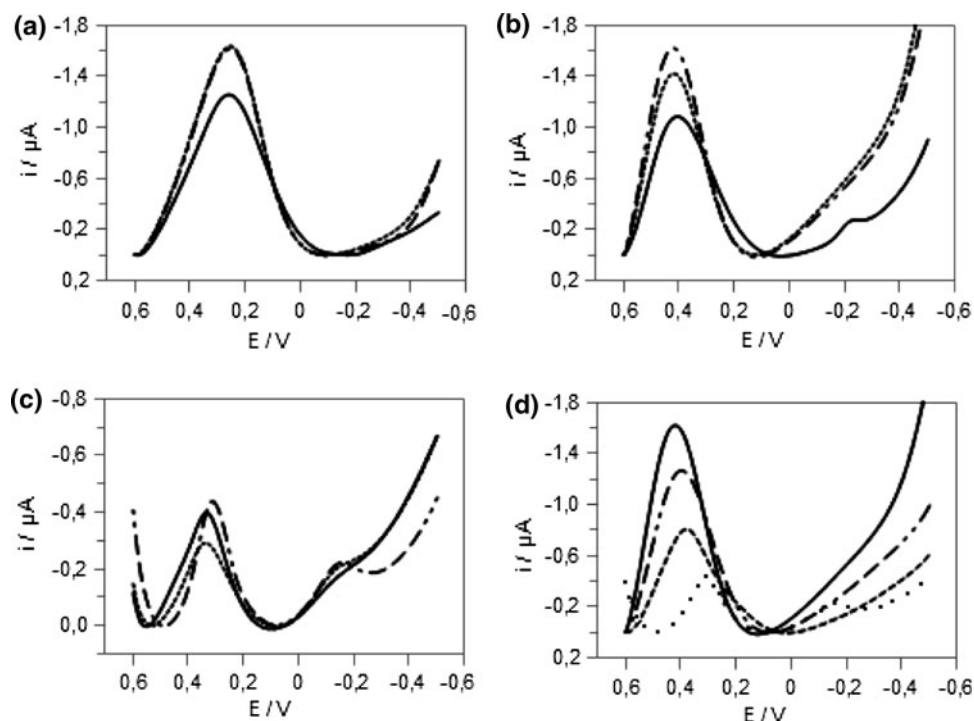
reversible oxidation was observed at +0.38 V, corresponding to the following reaction:

$$(Cor)H_3 \xrightarrow{-e} [(^\bullet Cor)H_3]^+ \rightarrow (^\bullet Cor)H_2 + H^+$$
$$(Cor)H_3 + H^+ \rightarrow [(Cor)H_4]^+$$
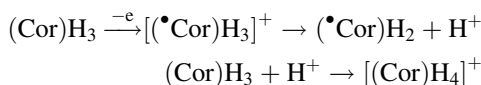
The reduction potentials of the neutral Fb corroles investigated by Kadish et al. were all reported to be below -1.0 V versus SCE, outside the stability window of our SAMs, and were thus not observed.

Determination of the surface pK_a

Electrochemical titrations were performed in a 0.1 M potassium phosphate buffered solution containing 1 mM $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ (1:1) as a redox probe. While we could not say from the onset which particular form of the corrole (protonated, neutral, or deprotonated) would be prevalent at which pH, the rate of electron transfer should decrease going from low to high pH due to increased inhibition as the electrostatic forces acting on the negatively charged redox probe change from more attractive to more repulsive (Fig. 3). This pH dependence of the redox marker was observed clearly in our experiments, with responses at high pH typically at 75–50% of those at low pH. Due to the low concentration of corrole on the electrode surface, a more complete blocking of the redox probe could not be expected.

The surface pK_a of a SAM can be calculated from the peak current of the OSWV scans at different pH, as the
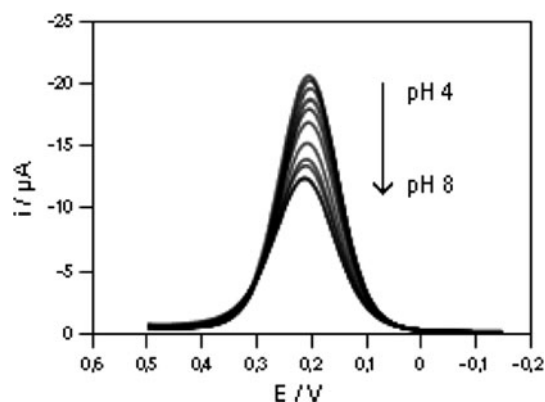

Fig. 3 OSWV spectra of 1 mM $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ in 0.1 M potassium phosphate buffer solution going from pH 4 to pH 8

redox current of the marker is dependent on the pH of the bulk solution. Following a paper by Dong et al. [30], the pK_a values were calculated as the pH values corresponding to a current equal to the average of the averaged currents at low and high pH. Accordingly, for a surface dissociation reaction

$$AH \rightleftharpoons A^- + H^+,$$

and the surface concentrations of the undissociated and dissociated end groups written, respectively, as [AH] and [A$^-$], with

$$[AH] + [A^-] = 1,$$

the pK_a of the acid can be calculated using the Henderson–Hasselbalch equation. Assuming the total apparent current

i to be composed of independent contributions from both [AH] and [A⁻], i can be written as:

$$i = i_A[A^-] + i_{AH}[AH]$$

The values of i_{AH} and i_A, the current values when the corrole is, respectively, fully protonated or fully deprotonated, can be obtained as the average values of i at both low and high pH. Combining these equations, we can obtain the following:

$$pK_a = pH + \log[(i_{AH} - i_A)/(i - i_A) - 1]$$

When [AH] = [A⁻], then pK_a and pH are equal to each other, and the last equation simplifies to:

$$2i = i_{AH} + i_A$$

From this, we could calculate the surface pK_a value of the SAM to be 6.4 ± 0.2.

Following the same procedure with the positively charged redox probe FcI, we could determine the surface pK_a of the corrole-containing SAM a second time, for a value of 6.7 ± 0.1. However, we must emphasize that the true redox probe turned out to be the iodide ion and not ferrocenyl. At the time of the experiment, we did not have a ferrocenyl compound with a redox-inactive counterion available, though undaunted by any knowledge of the redox behaviour of iodide we continued anyway. The values obtained were comparable to those obtained using the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ probe (Fig. 4), and a simple experiment using NaI as a redox probe confirmed that we were observing iodide. With this experiment we were able to confirm the surface pK_a once more with a value of 6.8 ± 0.2.

These pK_a values can be compared to the values obtained for similarly substituted corroles by Kadish and co-workers [41] using UV–Vis titrations in a non-aqueous solvent. While all corroles in their experiment were easily fully deprotonated using the strong bases piperidine and 4-aminopyridine (aqueous $pK'_a \sim 10$) in benzonitrile, complete deprotonation by the weaker bases pyridine or 2-amino-pyridine (aqueous $pK'_a \sim 6$) was only possible for particularly acidic corroles. A direct comparison between acidity equilibrium constants determined under widely differing conditions based on a very limited amount of data is of course difficult and must be done with caution, but still we can draw some conclusions.

Reported equilibrium constants by Kadish and co-workers [41] were 6.7 ± 0.7 for the deprotonation of the neutral corrole [(MePh)₃Cor]H₃, 6.1 ± 0.6 for [(NCPh)(Mes)₂Cor]H₃ (Mes = mesityl) and 4.0 ± 0.6 for the acidic corrole [(tpfp)Cor]H₃ (tpfp = tris(pentafluorophenyl)). Comparing this last value to the one obtained by Gross [25] for a similar corrole in aqueous solution (5.2), we can assume that the equilibrium constants for the two
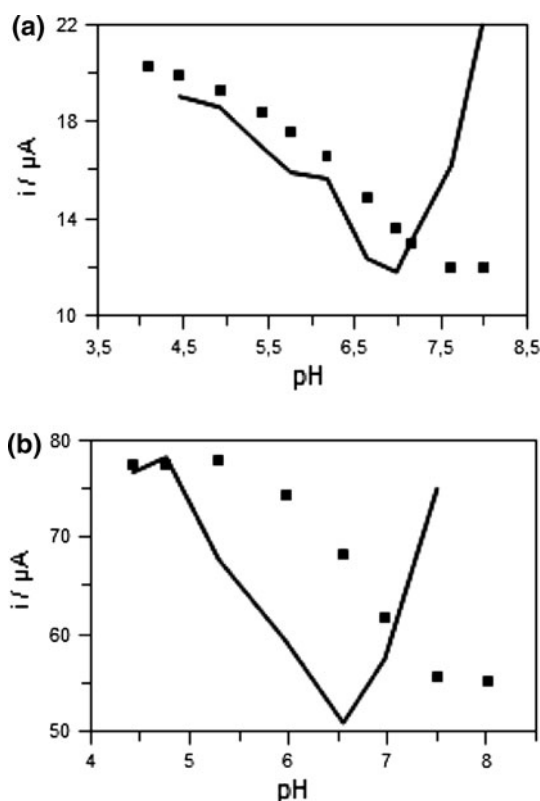

Fig. 4 Electrochemical titration curve (*filled squares*) and differential curve (*solid line*) using the **a** $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ and **b** FcI markers

neutral corroles under the same conditions would also be raised by a full pH unit. Combining this with the known fact that pK_a values of surface-confined acids usually are increased by 1–2 pH points, we can cautiously assume that the surface acidity of a neutral corrole should have a pH value of at least 8.5, and thus that the reaction we observed is, in fact:

$$CorH_4^+ \rightleftharpoons CorH_3 + H^+.$$

Attempts to confirm this hypothesis by determining the second pK_a value of the corrole were thwarted by the instability of the SAM, which was rapidly and irreversibly damaged by electrochemical measurements at pH < 3.5 and pH > 8.5. However, as most experiments and applications of SAMs performed in aqueous solutions fall within this pH range, this is only a minor inconvenience. An alternative method might have been the determination of the HOMO–LUMO gap of the surface-confined corrole at both low and high pH, as this is known to be dependent on the protonation state [26]. Unfortunately, as mentioned earlier, no reduction potentials could be obtained.

As the difference between the pK_a values for the first protonation and first deprotonation of a corrole is about 3 pH units, for some corroles both pK_a values will fall within

the SAM stability window. This would allow for the determination of both values in a single experiment and the unambiguous assignment of the corresponding acid–base equilibria. A concern at higher pH values is that any free (unreacted) amino functions in the SAM could start to influence the titration results, an effect which would be difficult to compensate for.

Conclusion

A free base corrole was incorporated into neat and mixed self-assembled monolayers, allowing for the measurement of its redox potentials using different electrolytes and at different pH values. The redox potentials were found to be a function of pH and the concentration of corrole on the surface.

An electrochemical titration method was used to determine the surface pK_a value of the free-base corrole. Three different redox probes, $K_3Fe(CN)_6/K_4Fe(CN)_6$, FcI and NaI, were used in the titrations, giving surface pK_a values for the corrole of 6.4 ± 0.2, 6.7 ± 0.1 and 6.8 ± 0.2, respectively.

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