



# Anion sensing with cobalt corrinoid grafted quartz crystal microbalances



Dilek D. Erbahar<sup>a</sup>, Ilke Gürol<sup>a</sup>, Felix Zelder<sup>b</sup>, Mika Harbeck<sup>a,\*</sup>

<sup>a</sup> TÜBİTAK Marmara Research Center, Materials Institute, P.O. Box 21, 41470 Gebze, Kocaeli, Turkey

<sup>b</sup> University of Zurich, Institute of Chemistry, Winterthurerstrasse 190, 8057 Zurich, Switzerland

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## ABSTRACT

Corrin macrocycles are well known for their interesting and multifaceted coordination chemistry at the axial positions of the cobalt center. In this work, the use of such cobalt corrinoids as sensitive elements for sorption based chemical sensors like the quartz crystal microbalance (QCM) is described for the first time. This approach of fast and reversible ion detection extends the versatility and applicability of this class of metal-containing ionophores and colorimetric indicators. QCMs were grafted with aquacyano and dicyano cobalt corrinoids and assessed in their sensing characteristics during exposure to cyanide, thiocyanate, and other ionic species as well as selected organic compounds. The liquid sensing characteristics of the corrinoids were found to be excellent. Sensors reach equilibrium in <3 s from the stable baseline after analyte exposure and the responses are fully reversible. Sensors of high sensitivity and selectivity for cyanide have been obtained with detection limits at 1  $\mu\text{M}$ . At the same time, the sensitivities to common organic compounds are negligible. The results demonstrate that corrin grafted QCMs exhibit enormous potential as chemical sensors for the detection of anions, especially cyanide, in aqueous samples.

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## 1. Introduction

Corrinoids exhibit interesting and multifaceted coordination chemistry at the axial positions of the cobalt center [1]. These macrocycles are especially known for their high affinity toward cyanide ions, but complexes with a variety of different axially bound ligands have also been described [2–4]. The electronic  $\pi$ – $\pi^*$  transitions of the tetradentate macrocycle are extremely sensitive to the nature and the number of axial ligands offering a versatile tool for analytical purposes [5]. Indeed, optical changes are already successfully utilized to quantify the presence of cyanide ions in solution by colorimetric detection [6–9]. Different cobalt corrinoids have also been immobilized in polymeric membranes as ion sensitive electrode materials. The electrodes showed high selectivities for nitrite [10,11].

The reversible interactions with cyanide and other chemical species of high interest in solution predestine corrinoids for the general use as sensitive elements on chemical sensors such as the

quartz crystal microbalance (QCM). The QCM is a versatile platform for rapid analysis of liquid and gaseous samples and commonly used in biosensor and chemical sensor systems. QCM sensors are well-established for the detection of pesticides, explosives, hydrocarbons, heavy metals or similar water pollutants [12–16], but until today a rather limited number of published works cover anion detection.

For cyanide detection with the QCM, the reaction of nickel with cyanide ions in the presence of oxygen was suggested causing a decrease in electrode mass and a positive frequency shift of the sensor achieving a lower limit of detection of 0.28 mg/l potassium cyanide [17]. In a similar approach using nano-sized silver particles a detection limit of 2.2  $\mu\text{g/l}$  was stated [18]. Using unmodified QCM gold electrodes detection limits of about 50  $\mu\text{g/l}$  potassium cyanide after 10 min analysis time and 2  $\mu\text{g/l}$  after 20 min analysis time [19] as well as 16.1 and 2.7  $\mu\text{g/l}$  for analysis times of 10 min and 1 h, respectively, were achieved [20]. Cyanide also promotes the disproportionation of Hg(I) and the consequent amalgamation of the mercury onto the gold electrodes leads to a frequency decrease. Concentrations in the range of 1–850 mg/l have been tested with the sensor [21].

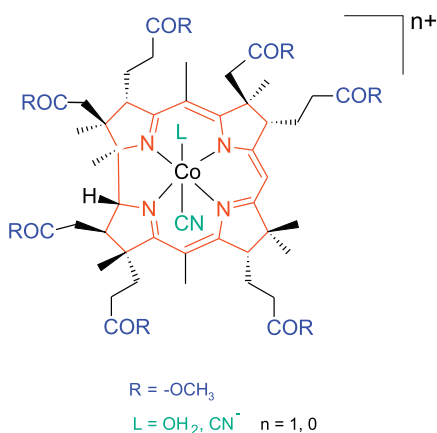
In addition to cyanide sensing, other anions such as thiocyanate [22] or iodine [23] were targeted using gold plated QCMs. The QCM was also applied to selenite [24], sulfate [25], and orthophosphate

\* Corresponding author. Tel.: +90 262 677 3123; fax: +90 262 641 2309.

E-mail addresses: [dilek.dundar@tubitak.gov.tr](mailto:dilek.dundar@tubitak.gov.tr) (D.D. Erbahar),

[ilke.gurol@tubitak.gov.tr](mailto:ilke.gurol@tubitak.gov.tr) (I. Gürol), [felix.zelder@chem.uzh.ch](mailto:felix.zelder@chem.uzh.ch) (F. Zelder),

[mika.harbeck@tubitak.gov.tr](mailto:mika.harbeck@tubitak.gov.tr) (M. Harbeck).



**Fig. 1.** Sketch of the chemical structure of the cobalt cobester complexes used for cyanide sensing with the QCM. The corrin macrocycle (red), the peripheral methyl ester substituents (blue), and the upper and lower axial ligands of the cobalt ion center (green) are indicated. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ions [26,27] with insoluble inorganic salts as sensitive compounds. Because of the chemical reactions or strong ionic interactions the time needed for analysis easily exceeds 10 min and sensor responses of the metal based sensors are non-reversible.

QCM sensors with an organic sensing element have been described in the detection of various cations or anions. Using dioctadecanoyl-cryptand-22 detection limits for ions and organic molecules were estimated at about  $10^{-5}$  M and  $10^{-4}$  M, respectively [28]. However, the sensor exhibits little selectivity as the development was targeted at a general ion chromatography detector. Similarly, a quartz crystal electrode coated with the crown ether sym-dibenzo-16-crown-5-oxydodecanic acid was prepared for the detection of various inorganic compounds [29]. A QCM was also employed to examine the inclusion of inorganic anions in a monolayer of  $\beta$ -cyclodextrin [30]. The organic sensitive elements produce fast and reversible sensor responses in contrast to the metal and inorganic salt based sensors described above; however, no such QCM based method for cyanide detection has been proposed yet.

In this work, aquacyano and dicyano cobalt corrinoid complexes having seven methyl ester functionalities are investigated with mass sensitive quartz crystal microbalance sensors and evaluated in their responses to aqueous samples containing different levels of cyanide, thiocyanate and other common anionic species as well as selected organic compounds. This is the first reported use of such cobalt corrinoid complexes as sensitive elements on chemical sensors. Based on the results, cobester grafted chemical sensors are proposed as an easy to use method for rapid and reversible detection of cyanide and other ionic species in liquids.

## 2. Experimental

### 2.1. Sensing materials

Corrinoids are cobalt complexes containing a macrocyclic corrin ligand at the equatorial positions and up to two additional ligands such as water or cyanide at the axial positions. In contrast to porphyrins, the A and D pyrrole subunits are directly connected as illustrated in Fig. 1. For the QCM sensor tests an amphiphilic cobalt corrinoid substituted with seven methyl ester groups (“cobester”) at the periphery of the macrocycle was synthesized in its dicyano and aquacyano forms as described previously [7,31].

### 2.2. QCM grafting with cobesters

Polished AT-cut quartz crystals with two asymmetric gold electrodes (10 and 5 mm in diameter) with a fundamental frequency of 4.95 MHz were used as transducers for the sensor tests. The cobesters were applied to the QCMs by spray coating a solution of the compounds in acetone (0.5 mg/ml). The resonant frequency was monitored continuously during the coating process and coating was ceased at a frequency shift of 500 Hz. The QCM were dried in a nitrogen stream before use.

Coating of the QCM with a 1-dodecanthiol monolayer was achieved in a self-assembly process by immersing an argon plasma pretreated crystal into a 0.8 mM solution of the thiol in 2-propanol for 3 h. Prior to use the coated crystal was rinsed with ultra-pure water and dried in a nitrogen stream. A frequency shift of about 100 Hz was recorded in air as the result of the self-assembled monolayer (SAM) formation.

### 2.3. Sensor test procedure

The QCM sensor signals were recorded with a QCMZ-500 system based on impedance analysis (KSV Instruments, Finland). All sensor measurements were made at a constant temperature of 20 °C due to the sensitivity of the QCM method to temperature. A detailed description of the system and procedures can be found in [32]. The fundamental QCM resonance frequency was used as sensor signal.

The inorganic salts and organic solvents for the preparation of the analyte samples were obtained from various suppliers in the highest available grade and used as received. Stock solutions of the analytes were prepared by adding 2 mg sodium cyanide, 100 mg sodium or potassium salts of thiocyanate, nitrite, nitrate, chloride, bromide, or acetate or 200  $\mu$ l of the organic amines triethylamine and *n*-butylamine and other organic compounds (*p*-xylene, tetrachloroethylene, chloroform, and acetonitrile) to 500 ml ultrapure water. The test samples were then prepared by diluting the stock solution to the desired concentration level just prior to the measurement. Sensors were first exposed to analyte free water until a stable baseline was obtained and then to the analyte containing sample waiting for equilibrium of the sensor. The sensors were regenerated finally by purging with analyte free water until the sensor signal returned to baseline level. This procedure was repeated for all concentration levels and analytes.

## 3. Results and discussion

### 3.1. Responses of unmodified and alkyl thiol SAM functionalized QCMs to ionic species

Previous studies of QCMs with bare gold electrodes have produced very diverging and inconsistent results in their responses to ionic species. The signal strength has been found to depend on the actual electrode geometry and is attributed to electro-acoustic phenomena such as interactions of electric stray fields between the two QCM electrodes with the conductive medium in contact with the QCM. For a recent discussion see [33,34] and the respective references therein. Besides, anions in solution might specifically or unspecifically adsorb on and interact with the gold surface of the electrode.

To investigate any possible influences on the sensor signal caused by direct interactions of the gold electrode with ionic or neutral analyte species in solution as well as any electro-acoustic contributions to the sensor signal, the responses of an unmodified, a 1-dodecanthiol SAM modified, and a 1-dodecanthiol SAM and cobester grafted QCM to diluted ion solutions and dissolved organic

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