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## Gas sensing with hexafluoroisopropanol substituted phthalocyanines and *vic*-dioximes: a comparative study

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**Abstract:** Phthalocyanines (Pcs) are established sensitive materials for chemical gas sensors due to their superb sensing characteristics and the achievable manifold in their analyte interaction properties. Their sorption properties are determined by the metal ion center and substituents attached to the periphery of the ring system. Similarly, *vic*-dioximes can be modified in their sorption properties and employed as sensitive materials. In this work, a nickel Pc and various *vic*-dioximes functionalized with the same hexafluoroisopropanol moiety are assessed and compared in their gas-sensing properties using the quartz crystal microbalance for the first time. This specific substituent is selected for its hydrogen bond acidity for strong interactions with analytes having corresponding sites. The synthesis and characterization of the new compounds are described. Sensor results are presented for ten selected organic compounds and the chemical warfare agent simulant dimethyl methylphosphonate (DMMP). Both compound classes exhibit good sensing performance but were found to exhibit very diverging analyte preferences, as preferential sorption of either amines or polar compounds was observed depending on the molecule type. Thus, by applying the same substituent to different base molecules, sensitive compounds with very distinct sensing properties can be realized.

**Key words:** Chemical gas sensing, quartz crystal microbalance, volatile organic compound, phthalocyanine, *vic*-dioxime, hydrogen bond acidity

### 1. Introduction

Chemical gas sensors have already found much attention as an analytical technique. Several major types exist, each of which is best suited for certain applications. Metal oxide reaction-based sensors are advantageous in the detection of small inorganic gases, whereas sorption sensors using sensitive organic materials are better suited for the detection of higher molecular weight volatiles. The latter are considered more selective while the former are generally more sensitive. The selectivity is governed by functional groups attached to the respective base molecule, e.g., a polymer backbone. These substituents are often selected to maximize the chemical interactions with the target molecules of interest, e.g., via hydrogen bonding.

Many organic molecules including phthalocyanines (Pcs) are known as excellent sensing materials next to polymers.<sup>1,2</sup> Pcs are macrocycles based on the porphyrin structure. Their two inner hydrogen atoms can be replaced by a metal ion and substituents may be added on the periphery. The type, position, and number of substituents and the choice of the center ion are influential factors for the gas sorption properties.<sup>3–5</sup> Analogous to Pcs, *vic*-dioximes are investigated as sensitive materials. *Vic*-dioximes are derivatives of glyoxime (ethanedial

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dioxime) featuring two neighboring oxime groups (=N-OH) that can be chemically modified by substituents in the 1,2 position and/or by forming metal complexes. *Vic*-dioximes in the free form with their native H bond acidity or as metal ion complexes exhibit varying preferences for different analytes depending on the substituents and the metal ion.<sup>6–8</sup>

H bond acidity can be introduced to a sensitive material by a variety of functional groups.<sup>9</sup> Among these, the hexafluoroisopropanol moiety is considered the most effective H bond donor in terms of H bond acidity and basicity. In most cases polymers are used as base compounds; however, Pcs and other compounds with this group are known as well.<sup>10–11</sup>

In this work, both Pcs and *vic*-dioximes with identical hexafluoroisopropanol-containing substituents are investigated in their responses to a wide range of organic volatiles including strong and weak H bonding partners using a quartz crystal microbalance (QCM). The test analytes comprise 10 selected organic compounds and the chemical warfare agent simulant dimethyl methylphosphonate (DMMP). The QCM is a common transducer platform for sorption type sensors and a reliable test tool for new sensitive compounds. The sensing properties are discussed in a comparison of the two different classes of sensitive compounds.

## 2. Results and discussion

### 2.1. Synthesis and characterization

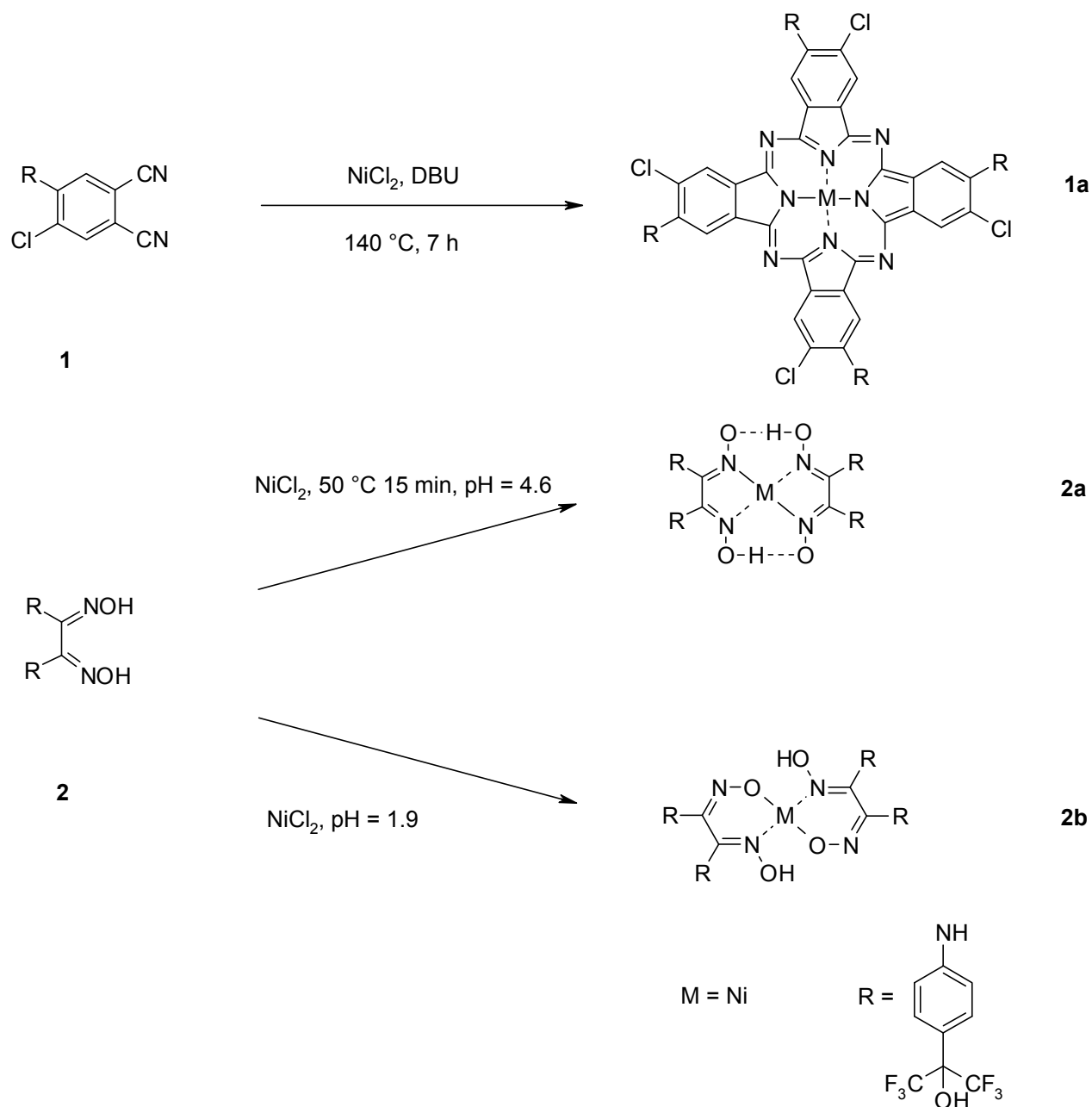
A nickel Pc (compound **1a**) and in total three different *vic*-dioximes (compound **2**) and *vic*-dioxime nickel complexes (compounds **2a** and **2b**) with the same hexafluoroisopropanol-containing substituent, namely 2-(4-aminophenyl)-1,1,1,3,3,3-hexafluoro-2-propanol, were synthesized to study their gas-sensing properties with the QCM. The synthesis pathways and chemical structures of the final compounds for the sensors tests and their substituents are presented in Figure 1.

The synthesis of the *Pc* and *vic*-dioximes followed established procedures described in the literature.<sup>8,12–14</sup> The chemical structures of the synthesized compounds have been confirmed using chemical analysis and spectroscopic methods.

### 2.2. General gas-sensing performance

The QCMs coated with the *Pc* **1a** and the *vic*-dioximes **2**, **2a**, and **2b** have been exposed to vapors of ten different organic compounds and DMMP at five concentration levels in a nonhumidified air stream to characterize their gas sorption and sensing performance. The selected analytes represent a wide range of chemical classes with very diverse sorption properties. In Figure 2 the simultaneous transient responses of the 10 MHz QCM transducers coated with **1a**, **2**, **2a**, and **2b** to pulses of ethyl acetate (EtOAc) and tetrachloroethylene (TCE) vapor of increasing concentration are presented as an example. The data are plotted without baseline correction; only the first sensor reading is used as zero reference and subtracted from all further data points.

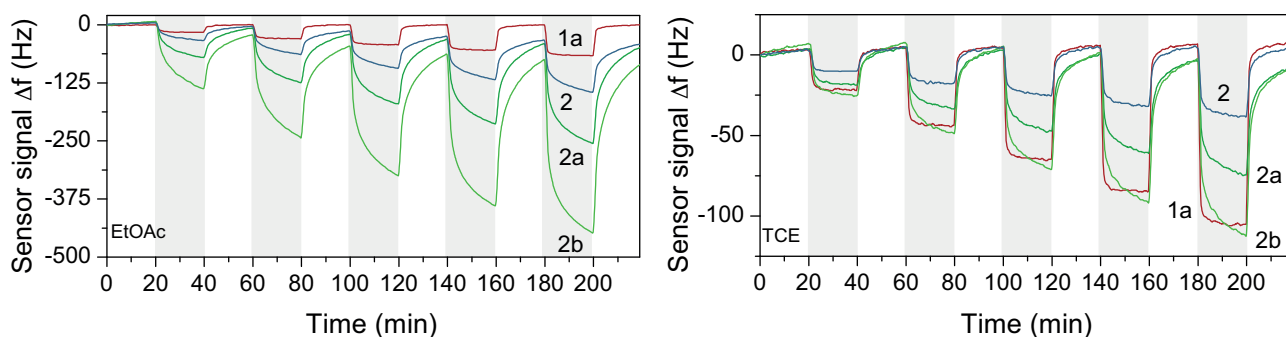
Generally, the gas sorption and sensing characteristics of the new sensitive compounds in terms of baseline stability, response and recovery times, and repeatability are good. The QCM sensors with **1a** and **2** exhibit the best sensing performance as judged by the quick responses and recoveries as well as the stability of the baseline. A slight decrease in the responses was observed during the first measurement directly after sensor preparation, but then the signals were stable over time in consequent measurements. The results shown and discussed here are the responses of the sensors after the initial stabilization phase. The initial decrease in the sensor responses was most notable for compounds **2a** and **2b**.



**Figure 1.** Synthesis pathways and chemical structures of Pc **1a**, *vic*-dioxime **2**, and *vic*-dioxime nickel ion complexes **2a** and **2b** studied in their gas sorption properties with the QCM in this work.

Response times ( $t_{95}$ ) for **1a** are typically in the range of 2–5 min and for **2** in the range of 4–8 min, but rather around 10 min for **2a** and **2b**. In the case of the analyte triethylamine (Et<sub>3</sub>N) response times are increased by 2–3 min for **1a**, while equilibrium is not reached within the exposure time window for the other sensitive compounds. However, a full recovery of the baseline is always observed.

The sensors' responses increase with increasing concentration of the analytes. The highest sensor responses were observed for the analytes EtOAc and acetonitrile (ACN). It can be noticed that the individual responses of the sensors differ much from each other for a given analyte. The diverging results for the four

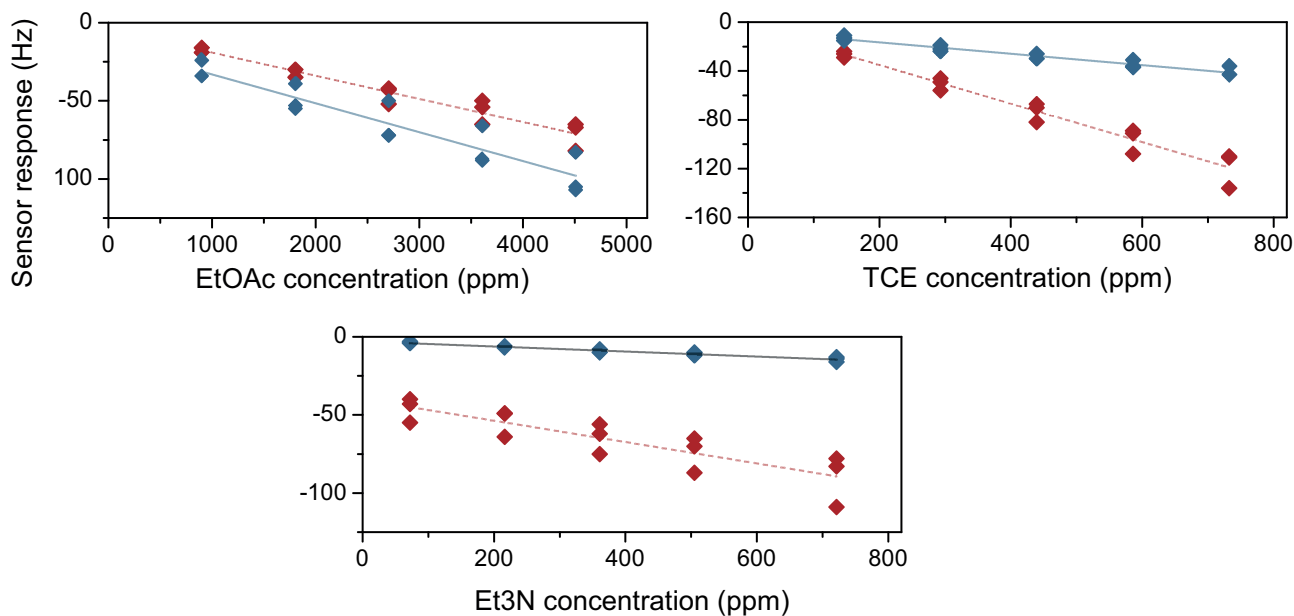


**Figure 2.** Transient sensor signals of QCMs coated with Pc **1a** (red line) and *vic*-dioximes **2**, **2a**, and **2b** (blue and green lines) during intermittent exposure to EtOAc (left, concentration 900–4500 ppm) and TCE (right, 150–730 ppm) vapors in dry air.

compounds show that the type of substituent bearing special functional groups is not the only major factor determining the gas-sensing properties of these types of sensitive compounds, but also the base molecule, i.e. Pc or *vic*-dioxime, plays an important role in the sensing mechanism.

### 2.3. Analysis of the sensor responses

The sensor response graphs in Figure 3 illustrate the concentration-dependent frequency shifts of the QCMs with **1a** and **2** to vapors of EtOAc, TCE, and Et3N obtained during three repeated measurements and the best-fit line. The responses increase with the concentration and no saturation effects are observed in the tested concentration ranges. The data were fitted using a two-parameter model including line slope and y-intercept. The sensor responses are highly correlated with concentration and  $r^2$  values are typically larger than 0.97.



**Figure 3.** Example sensor response curves for the analytes EtOAc, TCE, and Et3N of NiPc **1a** (red, dashed line) and *vic*-dioxime **2** (blue, solid line) including data of three repeated measurements.

The y-intercepts are considered mostly negligible, except for the test analyte Et3N (see Figure 3, bottom). For this analyte a dual model including Langmuir type adsorption is more suitable to cover the low concentration limit,<sup>15</sup> but the purely linear model can be applied with confidence over the mid to high concentration range.

From the model data partition coefficients have been calculated to describe the gas sorption performance of the new materials. Partition coefficients are the best performance indicators as they are independent of transducer and sensitive layer properties such as QCM resonance frequency, coating thickness, etc. The partition coefficient is defined as the ratio of the concentration of analyte molecules in the sensitive layer to the concentration in air. It serves as an indicator of analyte molecule enrichment in the sensitive layer and the sensors' sensitivities are directly related to the partition coefficients. The sensor responses after 20 min are used for analytes such as Et3N when no equilibrium has been reached.

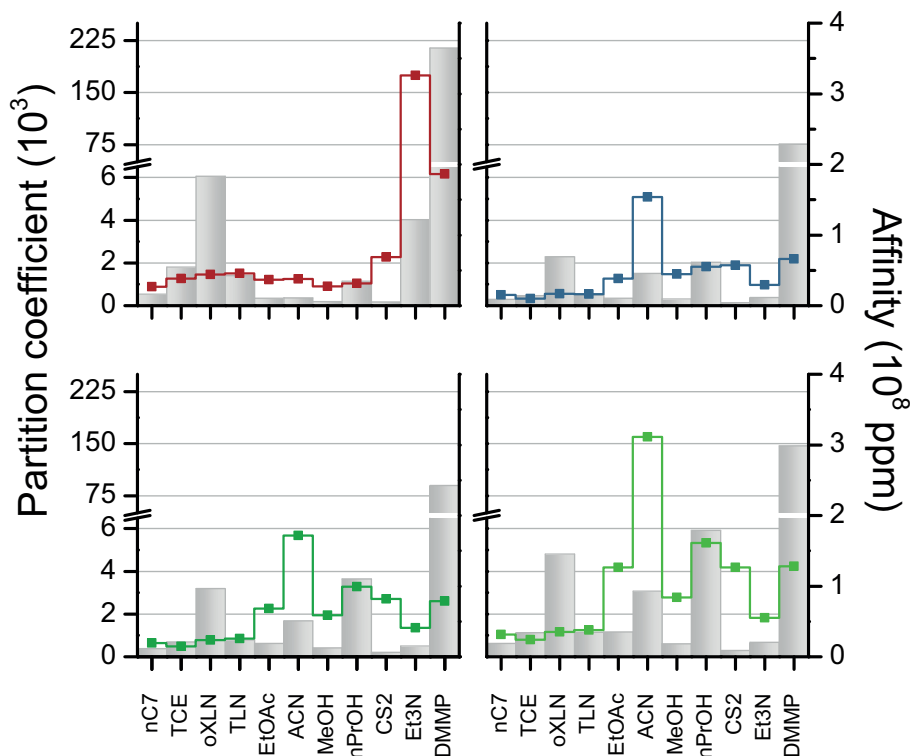
Along with the partition coefficients, affinities have been calculated from the sensor data. Affinities take into account the vapor pressure of the analyte. The lower the vapor pressure of an analyte, the higher the partition coefficient due to natural partitioning. Affinities can be used to compare the responses of a sensitive material to different analytes by eliminating this effect, revealing the real analyte preferences of the sensing materials. They are calculated from partition coefficients by multiplication with the saturation vapor pressure.<sup>8</sup>

In Figure 4 the partition coefficients and affinities are presented for the four sensitive compounds. The partition coefficients span a range from 140 for the analyte carbon disulfide (CS<sub>2</sub>) to 6000 for *o*-xylene (oXLN), whereas the values for DMMP are as high as 215,000. Compound **1a** has the highest partition coefficients among the sensitive compounds for the analytes TCE, oXLN, and toluene (TLN), as well as Et3N and DMMP, and at the same time the lowest for the polar compounds EtOAc, ACN, methanol (MeOH), and *n*-propanol (nPrOH). In contrast, all *vic*-dioximes exhibit high but varying sorption capabilities for the analytes oXLN, ACN, and nPrOH as well as DMMP. Among the *vic*-dioximes, compound **2b** shows the best overall sorption performance, while **2** has the lowest performance and compound **2a** is rather mediocre.

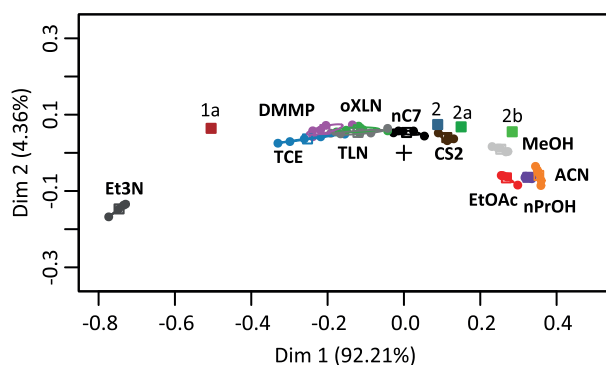
The affinities of  $P_c$  **1a** are uniformly low to most compounds, but it has a notably high preference for Et3N and DMMP. The affinities of the *vic*-dioximes indicate a high sorption preference for polar analytes such as EtOAc and nPrOH as well as CS<sub>2</sub>. At the same time, the affinities for Et3N and DMMP are quite low despite the rather high sensor responses. In all cases, the high responses to oXLN are mainly an effect of its low vapor pressure. The partition coefficient and affinity distributions of the *vic*-dioximes **2a** and **2b** are quite similar to each other and much related to the pattern of **2**, whereas the  $P_c$  **1a** has a very distinct pattern.

A more thorough analysis of similarities and differences can be achieved with principal component analysis (PCA): in Figure 5 the results of PCA using centered and normalized sensor response data to the different analytes are shown in a biplot of scores and loadings for the first two principal components. The ellipses centered at the sample means (represented by open squares) describe 95% confident regions. The data of each analyte are clustered without much spread. Most analyte clusters are well confined to a small area with only minor deviations along the concentration profile as expected from the high linearity of the sensor response curves. Clusters are mainly aligned along the first PC (DIM 1: 92% variance) according to the chemical nature of the analytes: polar analytes (alcohols, ACN, and EtOAc) are located on one side, hydrocarbons in the middle section near the origin, and high H bonding partners such as DMMP and Et3N on the opposite end.

The loadings reveal the sorption preferences and the similarities and dissimilarities of the sensing materials, and from the loadings the response profile in terms of selectivity/preference of a sensor can be derived. In the loadings plot sensors **2**, **2a**, and **2b** are positioned nearby and clearly apart from **1a**. Furthermore, **2a**



**Figure 4.** Partition coefficients (bars, left scale) and affinities (symbols, right scale) of the new sensing materials (**1a**, **2**, **2a**, and **2b**) for all analytes. Note: a break on the y-axes is introduced for partitions coefficients for the analyte DMMP.



**Figure 5.** Results of PCA showing the first two PCs in a biplot of scores (circles) and loadings (squares) obtained using the response data of the Pc and oxime-coated QCM sensors towards all tested analytes. Loadings are scaled to fit.

and **2b** are located in the direction of the polar analytes, being medium H partners ( $\beta = 0.33\text{--}0.48$ ), whereas **1a** is located on the opposite side towards Et3H and DMMP, both of which are strong H bonding partners ( $\beta > 0.79$ ).  $\beta$  is the parameter describing hydrogen bond basicity in the linear solvation energy relationship model.<sup>16</sup> Thus, compounds with the same substituent, such as **1a** and **2a/2b**, are found to have quite distinct sorption preferences.

Previously, the influence of the substituent has been utilized to obtain Pcs with varying sorption properties.<sup>17</sup> Pcs with high affinities for polar compounds have been obtained with fluoroalkoxy substituents, whereas alkyl substituted Pcs showed rather high responses to hydrocarbons. However, the hexafluoroiso-

propanol substituent used in this work is more effective in its interaction with many analyte molecules. Accordingly, higher partition coefficients for Et<sub>3</sub>N and nPrOH are observed than in the previous work. Recently, two different Pcs with the same substituent, but attached at different positions, have been studied in their responses to ten different VOCs.<sup>18</sup> The Pcs were found to exhibit quite high sorption capabilities of ethanol vapor and at the same time low sorption capabilities of triethylamine. The obtained partition coefficients vary in a broad range depending on the position of the substituent. Similarly, metal complexes of *vic*-dioximes have been studied in their responses to VOC vapors. The compounds show high affinity to alcohols depending on their chemical structure.<sup>7</sup>

However, phthalocyanines and oximes bearing the same substituent have not been investigated as of yet. For the first time, a direct comparison of a Pc with *vic*-dioximes having the same substituent is made. The results presented in Figures 4 and 5 reveal that the sensing properties are also notably determined by the molecule structure of the base compound—along with the structure, position, and number of the substituents as shown previously—based on the fact that Pc **1a** and *vic*-dioximes **2a**, and **2b** exhibit very different analyte preferences.

#### 2.4. Responses to water vapor

Humidity is a relevant factor influencing the performance of chemical gas sensors, and especially that of sorption-based sensors. Both the responses to water vapor itself, e.g., as a variation in humidity of the carrier gas, and the analyte sensing performance in the presence of humidity in the test samples determine the fitness of new materials for use as sensitive compounds in chemical sensors. Thus, the investigation of the humidity behavior of the new sensitive compounds was included in the test procedure as especially polar substituents or substituents bearing polar functional groups as used in this study may be prone to strong humidity influences.

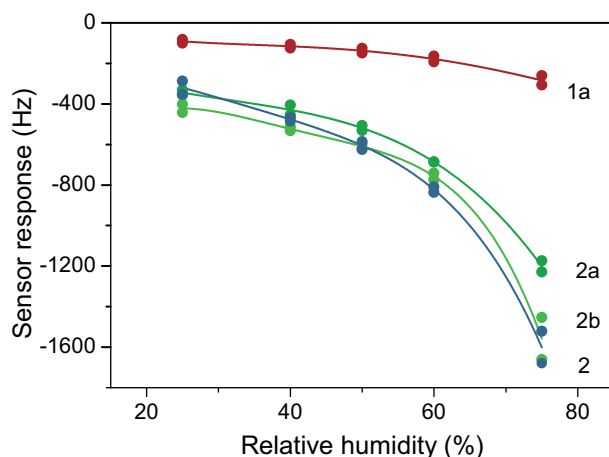
The responses to pulses of humidified air relative to the baseline obtained in dry air are very different for the four compounds under study. In Figure 6 the responses of the sensors to sudden pulses of humidified air ranging from 25% to 75% r.h. are depicted. Sensor **1a** is the least affected by humidity. The frequency shift for a change in humidity from dry air to a level of 75% r.h. is about 300 Hz. For low to medium humidity levels, the responses increase linearly with humidity, but for levels above 60% the responses are higher. The three oxime-based compounds show uniform behavior despite the differences in their chemical structure. The responses at 1600 Hz for the humidity shift from dry air to 75% r.h. are much larger than in the case of the Pc. However, the typical operation range of sensors in an application scenario under ambient conditions is between 40% and 60% r.h. and changes in humidity during measurements are generally much less severe, i.e. less than 10%. A change of 10% in the background humidity causes the sensors to drift on average as low as 30, 130, 120, and 170 Hz, respectively. If such changes occur over time, they can be nearly neglected for **1a** and easily compensated for the other compounds in common measurements scenarios.

#### 2.5. Analyte responses in humid ambient air

Studying the influence of humidity on the sensor responses is the second part of the humidity influence investigation. The same measurements as in dry air were conducted in a background of 50% relative humidity in the air stream to study the influence of humidity on the sensor performance. The sensors were found to be working in a humid ambience as well; however, the analyte responses differ from the dry air case to a varying degree.

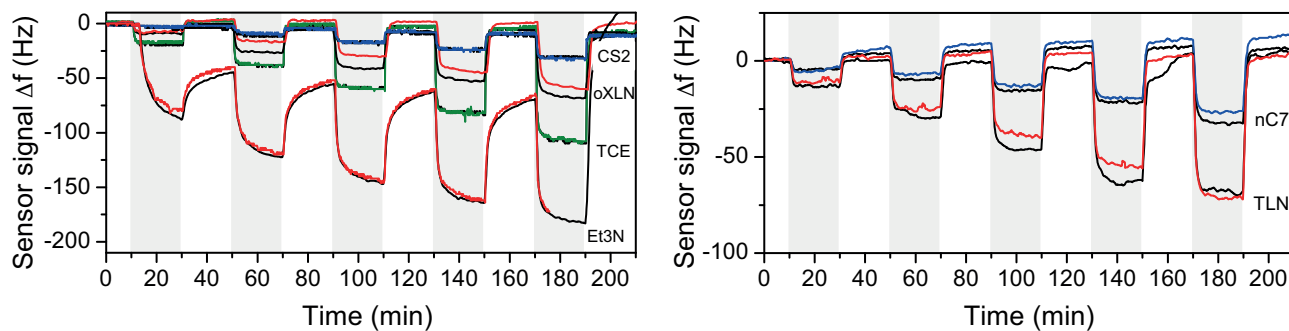
The response of a sensor with **1a** is depicted in Figure 7 in response to selected analytes in the presence





**Figure 6.** Responses of QCM coated with Pc **1a** (red line) and *vic*-dioximes **2**, **2a**, and **2b** (blue and green lines) during intermittent exposure to humidified air with humidity levels between 25% and 75% r.h.

of background humidity level of 50% r.h. in the analyte gas stream. The best results in humid air were obtained with the Pc **1a**. A decrease in the sensor responses compared to the dry air case was observed, but **1a** still exhibited an excellent performance, having a stable baseline, quick responses, and return to baseline closely following the gas concentration profile. The other materials, especially **2a** and **2b**, are considered less suitable for measurements at higher humidity levels. A general decrease in sensor responses was observed, whereas polar analytes such as ACN, EtOAc, and nPrOH give higher responses under the influence of humidity. However, the baseline tends to be less stable and the noise level increased.



**Figure 7.** Sensor performance in a humidity background level of 50% r.h. for a QCM with **1a** in response to intermittent exposure of the analytes TCE, oXLN, CS<sub>2</sub>, and Et<sub>3</sub>N (left) as well as nC<sub>7</sub> and TLN (right) in increasing concentrations.

## 2.6. Conclusions

A nickel Pc as well as a *vic*-dioxime and two nickel *vic*-dioxime complexes customized with the same hexafluoroisopropanol-containing substituent have been synthesized, investigated, and assessed in their analyte sorption and gas-sensing properties for the first time. Measurements with a wide range of selected test analytes have been conducted in dry and humid air using the QCM. The gas sorption and sensing performance of the phthalocyanine and *vic*-dioximes is discussed in a direct comparison of these two compound classes. The new sensitive materials show strong and stable responses to volatile organic compounds. The phthalocyanines and *vic*-dioximes have been found to be very different in their sensing properties despite bearing the same substituent. The Pc shows a high preference to amines and DMMP, while the *vic*-dioximes have higher affinities towards polar analytes

such as acetonitrile and n-propanol. The results demonstrate that sensor responses are strongly governed not only by the type and position of the attached substituents, as previously shown for Pcs, but also by the type of the base compounds. While both molecule classes can be used as sensitive coatings for chemical sensors, the results indicate that Pcs are more suitable than *vic*-dioximes, especially considering the performance at higher humidity levels.

### 3. Experimental

#### 3.1. Synthesis and characterization of the sensing materials

##### 3.1.1. 4-Chloro-5-{[4-(1,1,1,3,3,3-hexafluoro-2-hydroxy-propan-2-yl) phenyl]amino}phthalodinitrile (**1**)

2-(4-Aminophenyl)-1,1,1,3,3,3-hexafluoro-2-propanol (2.5 g, 9.65 mmol) was dissolved in 7.5 mL of dry DMF under an argon atmosphere and 4,5-dichlorophthalonitrile (0.76 g, 3.86 mmol) was added. After stirring for 10 min, finely ground anhydrous potassium carbonate (3.20 g, 23 mmol) was added in portions over 2 h with efficient stirring. The reaction mixture was stirred under argon atmosphere at 60 °C for 96 h. After cooling, water was added dropwise until a white precipitate formed. It was filtered off, washed with water, and then dried. Compound **1** is soluble in acetone. Yield: 40%; mp 98 °C; found: C 48.60, H 1.90, N 9.95; calc. for C<sub>17</sub>H<sub>8</sub>ClF<sub>6</sub>N<sub>3</sub>O: C 48.65, H 1.92, N 10.00; IR,  $\nu_{max}$  (cm<sup>-1</sup>): 3048, 3462 (NH), 3195 (OH), 2217 (C≡N), 1641, 1529, 1428, 1376, 1252, 1183 (C-F), 1135, 1113, 963, 940, 861, 701; <sup>1</sup>H NMR (acetone-d<sub>6</sub>),  $\delta$  (ppm): 9.50 (s, 1H, OH, disappeared upon D<sub>2</sub>O), 8.98–8.63 (d, 2H, Ar-H), 8.41–8.10 (d, 2H, Ar-H) 7.58 (s, 1H, Ar-H), 7.14 (s, 1H, Ar-H), 3.33 (s, 1H, NH); MS (ES), (m/z): 419 [M]<sup>+</sup>.

##### 3.1.2. 2,9,16,23-Tetrakis{[4-(1,1,1,3,3,3-hexafluoro-2-hydroxy-propan-2-yl) phenyl]amino}-3,10,17,24-tetrachloro phthalocyaninato nickel(II) (**1a**)

Compound **1** (0.180 g, 0.43 mmol), anhydrous NiCl<sub>2</sub> (0.013 g, 0.103 mmol), and DBU (0.1 mL) in 2 mL of *n*-amyl alcohol were stirred under argon at 140 °C for 7 h. The green reaction mixture was then poured into hexane (50 mL) and the resulting precipitate was filtered, washed with water, and then dried. The compound is insoluble in acetone. Compound **1a** is soluble in hot THF. Compound **1a** is obtained as an isomeric mixture. Yield: 17%. Found: C 46.90, H 1.80, N 9.65; calc. for C<sub>68</sub>H<sub>32</sub>ClF<sub>24</sub>N<sub>12</sub>O<sub>4</sub>: C 47.00, H 1.85, N 9.67; IR,  $\nu_{max}$  (cm<sup>-1</sup>): 3407 (OH), 1605, 1418, 1392, 1294, 1110 (C-F), 1080, 1072, 967, 888, 785, 750, 660, 618. MS (ES), (m/z): 1738 [M]<sup>+</sup>.

##### 3.1.3. N,N'-Bis[4-(1,1,1,3,3,3-hexafluoro-2-hydroxy-propan-2-yl)phenyl] diaminoglyoxime (**H<sub>2</sub>L**) (**2**)

Dichloroglyoxime (0.160 g, 1 mmol) was dissolved in 15 mL of absolute ethanol and was added dropwise to a solution of 2-(4-aminophenyl)-1,1,1,3,3,3-hexafluoro-2-propanol (1.04 g, 4 mmol) in 10 mL of absolute ethanol. The mixture was stirred overnight. Water was added dropwise until a white precipitate formed. It was filtered off, washed with water, and then dried. Compound **2** is soluble in acetone, DMSO, DMF, and THF. Yield: 56%; mp 67 °C; found: C 39.80, H 2.30, N 9.25; calc. for C<sub>20</sub>H<sub>14</sub>F<sub>12</sub>N<sub>4</sub>O<sub>4</sub>: C 39.88, H 2.34, N 9.30, IR,  $\nu_{max}$  (cm<sup>-1</sup>): 3400 (NH), 3200 (OH), 1610 (C=N), 1519, 1372, 1267 (C-F), 1186 (C-F), 1108, 963 (N-O), 931, 825,

705.  $^1\text{H}$  NMR (DMSO- $d_6$ ),  $\delta$  (ppm): 11.00 (s, 2H, NOH, disappeared upon  $\text{D}_2\text{O}$ ), 9.00 (b, 2H, ArCH-OH), 8.77–8.51 (d, 4H, Ar-H), 7.66–7.29 (d, 4H, Ar-H), 6.71 (s, 2H, NH); MS (ES), (m/z): 602.3  $[\text{M}]^+$ .

#### 3.1.4. N,N-Coordinated dimeric nickel complex [(E,E)-Ni(HL) $_2$ ] (2a)

To an ethanol solution (10 mL) of **2** (0.200 g, 0.34 mmol) an ethanol solution (5 mL) of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.040 g, 0.17 mmol) was added with stirring at 50 °C for 15 min. A distinct change in color and a decrease in the pH value of the solution were observed. An equivalent amount of KOH (0.1 m in EtOH) was added dropwise to maintain the pH value at 4.60 and a red precipitate appeared, identified as (*E, E*)-Ni(HL) $_2$ . The reaction mixture was cooled to room temperature. The red product was precipitated at 0 °C and filtered off, washed with water and cold ethanol, and then dried **in vacuo**. Compound **2a** is soluble in DMSO, DMF, and THF. Yield: 67%; mp 135 °C; found: C 38.00, H 2.00, N 8.80; calc. for  $\text{C}_{40}\text{H}_{26}\text{F}_{24}\text{N}_8\text{NiO}_8$ : C 38.10, H 2.08, N 8.88; IR,  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 3334 (NH), 3255 (OH), 1602 (C=N), 1519, 1363, 1212 (C-F), 1187, 1149, 962, 934 (N-O);  $^1\text{H}$  NMR (DMSO- $d_6$ ),  $\delta$  (ppm): 17.00 (s, 2H, O–H $\cdots$ O, disappeared upon  $\text{D}_2\text{O}$ ), 10.50 (s, 4H, ArCH-OH), 8.64–8.15 (d, 8H, Ar-H), 7.32 (s, 4H, NH), 6.70–6.63 (d, 8H, Ar-H); MS (FAB), (m/z): 1261.7  $[\text{M}]^+$ .

#### 3.1.5. N,O-Coordinated dimeric nickel complex [(E,Z)-Ni(HL) $_2$ ] (2b)

To a solution of **2** (0.200 g, 0.34 mmol) in 10 mL of warm ethanol,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.040 g, 0.17 mmol) in 5 mL of warm ethanol was added. The color changed from yellow to green and a decrease in the pH value of the solution to 1.90 was observed. After cooling to –10 °C, a yellowish-green precipitate formed. It was filtered off, washed with water and cold ethanol, and then dried **in vacuo**. The compound (E,Z)-Ni(HL) $_2$  is soluble in DMSO, DMF, and THF. Yield: 79%; mp 184 °C; found: C 38.05, H 2.05, N 8.80; calc. for  $\text{C}_{40}\text{H}_{26}\text{F}_{24}\text{N}_8\text{NiO}_8$ : C 38.10, H 2.08, N 8.88; IR,  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 3346 (NH), 3214 (OH), 1602 (C=N), 1518, 1371, 1206 (C-F), 1182, 1149, 968, 932 (N-O);  $^1\text{H}$  NMR (DMSO- $d_6$ ),  $\delta$  (ppm): 11.00 (br, 2H, OH, disappeared upon  $\text{D}_2\text{O}$ ), 8.64–8.48 (d, 8H, Ar-H), 7.58 (s, 4H, NH), 7.24–7.14 (d, 8H, Ar-H), 6.69 (s, 4H, ArCH-OH); MS (FAB), (m/z): 1261.7  $[\text{M}]^+$ .

### 3.2. QCM sensor preparation

AT-cut quartz crystals of 10 MHz fundamental frequency (Klove Electronics B.V., the Netherlands) were used as transducers for testing the new sensitive materials. With the help of an airbrush coating system the sensing materials were deposited from THF solution on both sides of the transducer. During the coating the frequency of the QCM was monitored and coating was stopped when a frequency shift of 11 kHz was reached (each side). Compound **1a** was coated at 16 kHz only. Sensors were freed from remaining solvent in a dry air stream prior to use.

### 3.3. Sensor test procedure

An automated gas mixing system with computer controlled mass flow controllers providing carrier gas, humidified air, and carrier gas saturated with analyte vapor was used for the preparation of the analytes. Saturated gas vapors are produced by vaporizers filled with the liquid analyte and immersed into a thermostated bath. The gas composition is adjusted by adding different levels of the saturated analyte vapor to the carrier gas stream while keeping the total gas flow constant at 200 mL/min. The humidity level of 50% r.h. was adjusted similarly. Typical experiments consist of repeated exposure to analyte gas (20 min) and subsequent purging with pure air

to reset the sensors' baseline. The sensing materials were characterized using a wide selection of organic volatile compounds comprising the alcohols MeOH (1000–5000 ppm) and nPrOH (130–650 ppm), as well as EtOAc (900–4500 ppm), Et3N (70–750 ppm), ACN (950–4700 ppm), CS2 (500–5000 ppm), and DMMP (0.3–3.0 ppm). The sensors were also exposed to vapors of the aliphatic or aromatic hydrocarbons *n*-heptane (nC7, 380–1900 ppm), TLN (240–1200 ppm), oXLN (40–200 ppm), and chlorocarbon TCE (150–730 ppm). These test analytes were selected to represent common chemical classes and a wide range of chemical properties as expressed in linear solvation energy relationship parameters.<sup>16</sup> The concentrations correspond to levels between 5% and 25% of the vapor pressure of the respective analyte at –10 °C in five concentration steps calculated using Antoine's equation.<sup>19</sup> During the measurement the sensor chamber was kept at 22 °C at all times. The sensors with different sensitive materials were placed in the same measurement cell and always characterized under identical conditions. Measurements were repeated at least three times.

Selectivity is a measure for the extent to which a sensor responds to a particular analyte in relation to the responses to other analytes. It can be calculated as the ratio of the sensor sensitivities for two test analytes. Sensitivity is the change of the sensor signal per analyte concentration unit, i.e. the slope of the calibration graph. It is obtained by a linear best-fit to the sensor responses as a function of analyte concentration.

The response time is generally defined as the time required for a sensor signal to change from its baseline value to the equilibrium level during gas exposure. A similar definition is made for the recovery time, when the sensor signal returns from the equilibrium level to the baseline after switching to the carrier gas stream without analyte. In this work response times (denoted as  $t_{95}$ ) are based on the time to reach 95% of the full equilibrium response or to reach the baseline within 5% of the initial value.

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