Chemosensors

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Chemical Sensing with Familiar Devices**

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Computers and mobile phones are ubiquitous devices that are continuously evolving and becoming ever more sophisticated. Eventually, they will constitute a global network of casual terminals that are geographically traceable and able to capture images and sounds of increasing quality. Other target inputs such as odors[1] or (bio)chemical parameters[2–4] are, however, more difficult to detect on such a massive scale, particularly with a generic type of instrumentation. Such a possibility would enable, for example, health diagnostics, environmental monitoring, and food quality assessments on a personalized level and also to feedback determinations of the same parameters to the network. Certainly, it would be a significant advantage if this was feasible as a natural extension of the capabilities of familiar and already well distributed devices.

Here we demonstrate the analytical capabilities of a regular computer screen with a web camera[5,6] for detecting and recognizing different molecules with an inexpensive (and eventually disposable) optical-sensing interface. By using semitransparent spots of porphyrins[7] as sensors we show that is possible to detect detailed and partially disentangled absorption and emission responses resulting from molecules such as amines, CO, and NO_x. The current system is also representative of other sensing approaches that use arrays of fluorescent indicators, and highlights the possibility of analyzing complex response patterns with available means.

Computer screens are not only our main computer interface, they are also widely configurable solid-state light sources.[8] They are capable of displaying confined areas of arbitrary shape, color, and intensity that can be two-dimen-

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sionally scanned on the screen with 200 μm resolution. All of this is achieved without moving parts and eventually has the possibility of becoming portable, as in the case of LCD displays in cellular phones. It is also true that they are not the natural choice of light sources for analytical purposes; however, they are everywhere and always inherently combined with substantial computing power, and their versatility and processing capabilities allow many of their weaknesses to be overcome. This aspect has been recognized and exploited in the so called computer screen photoassisted technique (CSPT)[5,9,10] for optically characterizing arrays of target indicators.

Here we demonstrate a disposable array of sensing substances that responds with a variety of absorption and emission changes that can be characterized by CSPT. The ability of the system to generate and analyze complex response patterns enables sophisticated determinations using an available and globally disseminated infrastructure (for example, computer sets).

Color arrays are common in biosensing applications,[2,3,11] but there are also examples of optical electronic noses[1,4] and electronic tongues.[12] The research group of Suslick, as well as others, have demonstrated that arrays of porphyrins are a feasible alternative for detecting gases and organic vapors[4,13–16] with minimum instrumentation (for example, reading the responses with flat-bed scanners[17]).[4] Here such a molecular system is chosen because of its rich variety of spectral responses that are used to test the method and to exemplify its possibilities for evaluating fluorescence-labeled assays in general. We thus made experiments on spots of thin layers of (5,10,15,20-tetraphenylporphyrin)zinc ([Zn(tpp)]), (5,10,15,20-tetraphenylporphyrin chloride)iron ([Fe(tppCl)]), and 2,3,17,18-tetraethyl-7,8,12,13-tetraamethyl-*a*,*c*-biladiene dihydrobromide (BD) dispersed in a polyvinylchloride (PVC) matrix and spotted in duplicate on a glass slide (inset in Figure 1 a). The sensing array was exposed to low concentrations of molecules such as NH_3, NO_x, CO, and triethylamine (TEA) in nitrogen.

Computer screens are able to display more than 16 million colors that are formed by different weighted combinations of red, green, and blue primary spectral radiances (RGB colors). During a CSPT measurement a web camera captures the image of the array under an illuminating sequence provided by the screen (a rainbow of 50 colors in this study). From this video stream regions of interest (ROI) are selected (the white circles in Figure 1 a) and used to compose substance fingerprints. The changes in the intensity (average of all the pixels in each ROI) recorded in the channels of the web camera with respect to the intensities recorded in pure nitrogen are shown in Figure 1 a. Signals from the red, green, and blue channel are concatenated in this order, and the fingerprints of all the spots are composed in a single fingerprint of the array (Figure 1 a). The intensity measured, for example, in the red channel of the web camera, for an illuminating color *i* defined by the triplet (r_i, g_i, b_i) is given by Equation (1).

$$I_{Ri} = \int_{\lambda} [r_i\, R(\lambda) + g_i\, G(\lambda) + b_i\, B(\lambda)]\, S(\lambda, i)\, F_R(\lambda)\, D(\lambda)\, d\lambda \qquad (1)$$

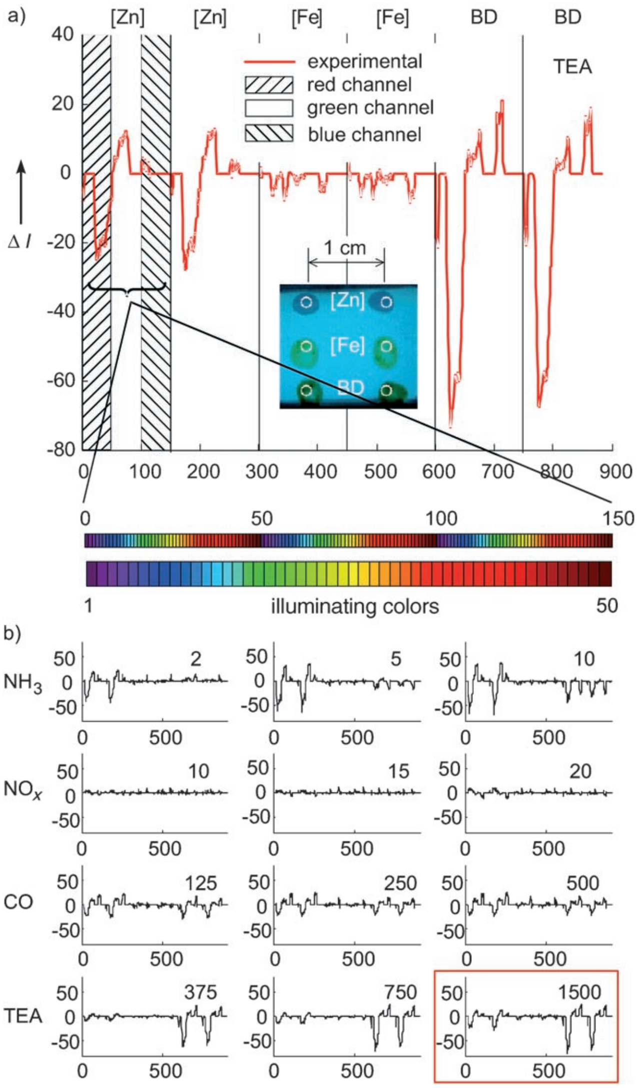

Figure 1. a) CSPT fingerprint of 1500 ppm of triethylamine (TEA). The data correspond to absorption/emission changes of the indicator spots upon exposure to TEA observed as intensity changes in the red, green, and blue channels of the web camera for different screen illuminations. These results were obtained from exposure, at room temperature, of the array to 1500 ppm of TEA in N_2 with the signal of N_2 subtracted. Each spot becomes represented by 50 values in the red channel, 50 values in the green channel, and 50 values in the blue channel. The units on the *y* axis are in "intensity level changes" of the web camera signal (that is, between −255 to +255)). The numbers on the *x* axis identify illuminating colors for the three camera channels and for the six imaged spots. All 900 points were obtained during one single run of the illuminating sequence of 50 colors (ca. 50 s measurement). The inset shows an image of the array at one given color frame ("blue") on the computer screen. The circles illustrate "the regions of interest" (ROIs) used to calculate the average intensity of the light reaching the web camera through the indicator spots. The illuminating sequence used (colors 1–50) as well as the concatenation of the camera channels to construct the fingerprints of a particular spot are shown. b) CSPT fingerprints of a number of molecules at different concentrations obtained with the array of porphyrin spots (inset Figure 1 a). [Zn] = [Zn(tpp)], [Fe] = [Fe(tppCl)], BD = biladiene.

The spectral radiances of the screen primary colors ($R(\lambda)$, $G(\lambda)$, and $B(\lambda)$) are polychromatic sources illuminating the

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tested substance,[6] and represented by $S(\lambda, i)$, which accounts for the substance transmittance $T(\lambda)$ and emission ($E(\lambda,i)$) spectra weighted by the spectral composition of the illumination.

The red, green, and blue filters of the web camera and the spectral response of the detector are represented by $F_R(\lambda)$, $F_G(\lambda)$, $F_B(\lambda)$, and $D(\lambda)$, respectively. Equation (1) summarizes the way that CSPT perceives the excitation emission characteristics of the tested substances when illuminated by the polychromatic light provided by the screen.

Figure 1 b collates the response features from different concentrations of target stimuli. The different features of the results in Figure 1 b are understood from the corresponding absorption and emission changes of the different porphyrins resulting from the target molecules, and are related to shifts in the absorption and emission peaks, as well as changes in the peak sizes and widths. The ability of CSPT as a method for practical evaluations depends on how well the fingerprints in Figure 1 b distinguish different molecules. A simple and efficient way to summarize and compare information in complex signals is to apply principal component analysis (PCA) to the fingerprints.[18,19] Figure 2 a shows the first two principal components of the whole set of fingerprints which explain about 80 % of the original information. This plot shows the classification of the considered molecules for the different tested concentrations. The biplot representations in Figure 2 b and c address the correlation of the classification with the source of the CSPT signals. In these graphics, scores that are 100 % correlated with a measuring condition lie in the same direction, while perpendicularly oriented elements are not correlated. Thus, it is possible to identify the CSPT measuring conditions that determine the ability of the CSPT fingerprints to distinguish the different target stimuli. For example, NH_3 detection is mainly correlated with the [Zn(tpp)] response observed in the red channel (Figure 2 b), which identifies changes in the emission, whereas the blue channel recognizes CO (Figure 2 c). Similarly, the detection of TEA is correlated with the quenching of the BD fluorescence (Figure 2 b). From Figure 2 it is also possible to identify a subset of optimum illuminating conditions that could produce a similar result with a shorter color sequence, an important aspect for implementing fast measurements or determination based on mobile phones instead of computer sets.

In this work we selected Zn– and Fe–metal complexes of tpp and a linear tetrapyrrole (BD). In the case of metalloporphyrins, the coordination of the analytes to the metal center is the expected sensing mechanism; aggregation of macrocycles or other matrix effects are ruled out by the dispersion of the porphyrins into the PVC membrane. We selected Zn and Fe complexes because they are representatives of two broad classes of porphyrins according to Gouterman's classification:[7] [Zn(tpp)] represents a "regular" porphyrin, while [Fe(tppCl)] is a typical "irregular" porphyrin. As an important consequence for CSPT applications, [Zn(tpp)] produces fluorescence emission, while [Fe(tppCl)] is a radiationless substance.

In the case of [Zn(tpp)], coordination at the metal center generally induces a red-shift of both the absorbance and emission bands, together with a significant quenching of the fluorescent emission[20] (which is observed as a negative peak in the red channels for a blue illumination, see for example Figure 1 a). All these features are well represented in the CSPT results by positive and/or negative peaks arising from

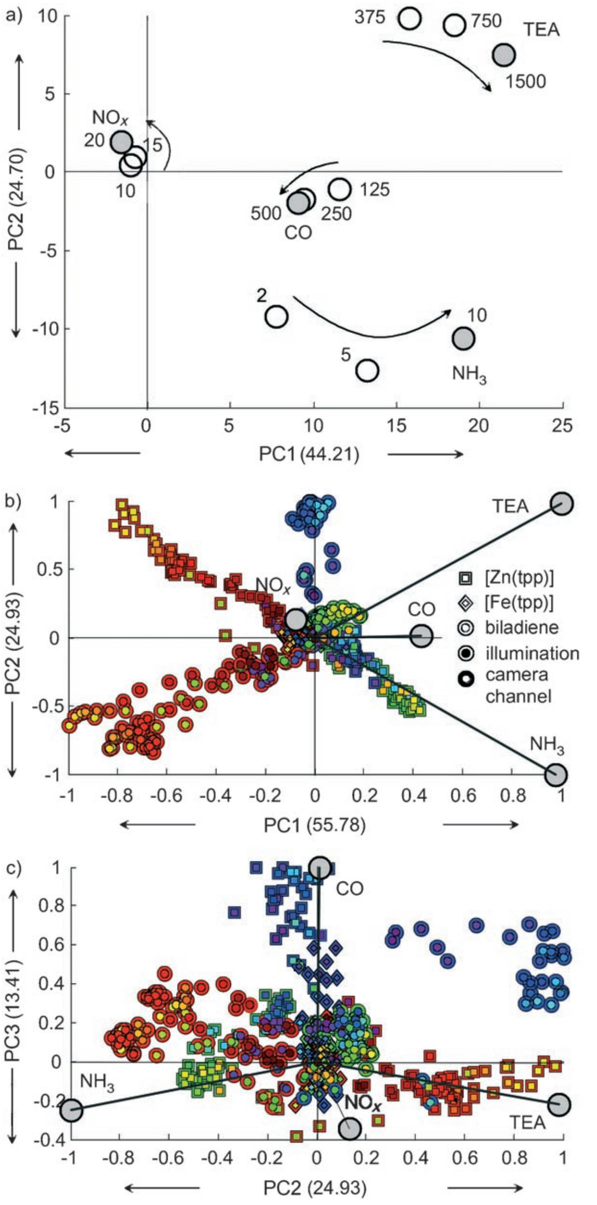

Figure 2. a) Principal component analysis[18] (PCA) of the results in Figure 1 b. The intensities in the three channels were made into a data set consisting of 900 points for each measurement and evaluated by standard PCA. The scores plot shows the classification properties of CSPT. The arrows indicate the evolution of the points in the score plot for increasing concentration of the target gases. b) and c) Biplots corresponding to the largest concentrations of the tested gases. The results are shown as PC2 versus PC1, and PC3 versus PC2. In the biplots the contribution from the different colors of the illumination (inner color of the symbols), the camera channels (outer color of the symbols), and the different indicators (□, ◇, and ○ for [Zn(tpp)], [Fe(tppCl)], and BD, respectively) are indicated. The gray circles show the PCA scores of the different molecules. The colored symbols (the loads) indicate the contributions to the scores plot, and thus their relative weight in the classification of the molecules.

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predominant absorption and/or emission responses, respectively. In the case of [Fe(tppCl)], the "irregular" absorbance optical spectrum gave less evident changes in the CSPT responses and this feature, together with the lack of emission, results in smaller responses (Figure 1 b). A completely different sensing mechanism should be considered with BD; the linear tetrapyrrole is stable as a dication and its interaction with bases induces significant changes in the molecular structure and consequently in the optical spectra. Loss of a proton leads to the formation of the 22,24-*a*,*b*,*c*-dihydrobilatriene hydrobromide and the loss of a further proton to the corresponding free base, with color changes from red to yellow-orange to green. In solution the formation of the BD free base leads to the formation of corrole by a ring-closure reaction.[21]

In the CSPT measurements we observed an unexpected reversibility of the BD layers upon interaction with TEA or NH_3. Concurrent spectral analysis of a model system suggests that the cyclization reaction does not occur so rapidly in the PVC membranes. From the CSPT results a significant variation in fluorescence after interaction, for example, with amines, even stronger than those obtained with [Zn(tpp)], was expected and corroborated by emission/absorption spectroscopy.

In this study the feasibility of ubiquitous environmental monitoring using an assembly of familiar devices already globally distributed has been demonstrated. This was done with a proven disposable chemical interface but measured with a detail not intuitively expected for the involved instrumentation and not readily available by any other method on the scale considered.

Since it will eventually be possible to run CSPT experiments just through an internet browser, such instrumentation would give a new dimension to environmental monitoring, food quality control, and also medical diagnostics at places where conventional analytical instrumentation would be either too expensive and/or requiring non-available expertise.

The recent introduction of global satellite imaging in search engines,[22] where the location of the user can be detected and placed in the geographical context of the search, is an ongoing vision that could naturally incorporate randomly read environmental or sanitary evaluations performed by the users of CSPT setups. When it is considered that these evaluations can take place everywhere, even in locations inaccessible to remote sensing, for example, inside buildings, they could supply global monitoring with a substantial degree of detail just by exploiting the chemical senses of familiar devices.

Experimental Section

Metalloporphyrins and BD were prepared according to a literature method.[23] The array was prepared by deposition of drops of PVC membrane solutions (1 wt% of porphyrin, PVC/bis(2-ethylhexyl)sebacate (1:2) polymeric matrix) in tetrahydrofuran onto glass slides. Evaporation of the solvent led to the formation of a PVC/porphyrin membrane. Two spots of each porphyrin were made as illustrated in the inset of Figure 1 a to test the reproducibility of the method.

The glass slide with the printed sensing array was introduced into a gas cell with glass walls, where it was exposed to controlled concentrations of different gases with the aid of an automatic gas-mixing system.

The measuring procedure used is standard to CSPT experiments and can be found elsewhere[5] and involves a regular LCD screen (Philips 170S4) used as a light source and a Logitech Quickcam pro 4000 operating at a resolution of 320 × 240 pixels used as the image detector. A sample holder such as that described in Ref. [10] provides a controlled geometry for the measurements, and shields the experiments from ambient illumination.

Software written by us in Matlab commands the measurement procedure (illuminating sequence and video acquisition) and extracts the information (CSPT fingerprints) from manually selected ROIs (white circles in the inset Figure 1 a).

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