

# Colour Catcher<sup>®</sup> Sheet Beyond the Laundry: a Low-cost Support for Realizing Porphyrin-based Mercury Ion Sensors

Fabrizio Caroleo,<sup>a</sup> Gabriele Magna,<sup>a</sup> Caterina Damiano,<sup>b\*</sup> Matteo Cavalleri,<sup>b</sup> Emma Gallo,<sup>b</sup> Corrado Di Natale,<sup>c</sup> Roberto Paolesse<sup>a</sup>

<sup>a</sup> *Department of Chemical Science and Technologies, University of Rome Tor Vergata, Rome, Italy.*

<sup>b</sup> *Department of Chemistry, Università degli Studi di Milano, Milan, Italy.*

<sup>c</sup> *Department of Electronic Engineering, University of Rome Tor Vergata, Rome, Italy.*

## ***Abstract***

The detection of mercury ions in drinkable water is a challenging task, because this heavy metal should be detected in very low concentrations. While analytical laboratory instruments can allow reaching the required sensitivity, the need of continuous monitoring of water samples by chemical sensors is more difficult. In this work we report the development of a simple colorimetric approach, based on the color variation of a free base porphyrin upon interaction with Hg(II) ions. The support is made by Colour Catcher<sup>®</sup> strip embedded by the tetra (4-carboxyphenyl)porphyrin; the anionic character of the porphyrin allows a uniform and stable deposition onto the positively charged solid support. An optical platform, composed by commercial electronic devices, such as LED and web cam, coupled to a PC has been developed to digitalize the images of the strip color changes upon the flux of water solution containing Hg(II) ions. Homemade software developed in Matlab, using the Hue parameter, was exploited to analyze the color changes, allowing reaching a LOD three times below the Hg(II) legal limit stabilized by WHO. The device also showed a good selectivity towards other potential interferent metal ions, demonstrating the potentialities of this approach in the real field.

## **Keywords**

Chemical sensors; optical sensors; colorimetry; porphyrins; heavy metals; drinkable water

## **Highlights**

- Colour Catcher<sup>®</sup> is a cheap and functional solid support for dyes
- Porphyrins reversibly interact with Hg(II) ions undergoing color changes
- Cheap electronic devices are used to develop an optical sensor platform
- Detection of Hg(II) below the WHO limit is reached in water samples

## Introduction

The access to drinkable water is nowadays an important issue, due to the potential sources of pollution from anthropogenic as well as natural sources [1]. Among inorganic pollutants, heavy metal ions play an important role for their harmful effects on the environment and human health [2], because their extensive uses in different fields of applications led to their spread in the environment, with the consequent accumulation in humans [3]. Among the different heavy metals, mercury has been one of the most studied, because of its diffused use and toxicity; the intake of high doses of mercury can induce in humans' abdominal colic pain, bloody diarrhea, kidney failure and brain damages [4], while a continuous intake of low doses of mercury can lead, after a long period of time, to several dangerous health complications altering brain functions: neuropsychiatric disorders including fatigue, anxiety, memory problems and detrimental impacts on intellectual function in children [5]. The World Health Organization's (WHO) in 2017 has established a very low value equal to 0.006 mg/L ( $[\text{Hg}^{2+}]_{\text{max}} \approx 3 \times 10^{-8} \text{ mol L}^{-1}$ ) as the legal limit of mercury allowed in drinking water [6].

This low concentration limit generally restricts the possibility of Hg(II) detection to the use of analytical chemistry instrumentations, but these protocols prevent the possibility of in-field continuous monitoring of water sources due to both the time necessary to analyze the sample and the relative cost of these analyses.

To overcome these limitations, the development of low cost, sensitive and easy to handle devices is nowadays required [7]. A great interest has been devoted to the realization of optical sensors, because these devices can possess fast response, good sensitivity, low costs of their realization, the simplicity of their use and easy signal acquisition [8], which can satisfy the requirements for prompt in-field analyses of water samples.

Furthermore widely distributed electronic devices, such as smartphones and webcam, can be exploited to develop cheap sensing platforms, making optical sensors easily available for practical applications [8,9]. In some cases, even "naked-eye" detection can be possible, simplifying even more the operation mode.

Porphyrins have been widely exploited as sensing materials in optical sensors, because of the richness of their photophysical properties and the possibility to tune them by synthetic modifications [10]. Furthermore porphyrins are also versatile chelating systems, able to host several ions in their binding pocket, and for this reason they are powerful receptors to detect cations in a complex matrix [11,12] and develop optimized optical sensor arrays.

The coordination of a Hg(II) ion into the porphyrin core, for example, induces important variations in the UV-Vis spectrum of the macrocycle, making a strong color variation that is observable by naked eye [13].

The deposition of the sensing material onto a suitable solid support is a key step to develop a suitable optical sensor and in literature is reported the use of  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  core magnetic microspheres to immobilize 5-(4-aminophenyl)-10,15,20-triphenylporphyrin for Hg(II) ion detection [14]. While this system appears to have excellent selectivity for the detection of mercury ion in view of the colorimetric variation from reddish to the green color when exposed to mercury ions in solution, sensitivity results not suitable for the detection of trace amounts of  $\text{Hg}^{2+}$ , since no color change was observed when the concentration of  $\text{Hg}^{2+}$  is lower than  $4 \times 10^{-5} \text{ mol L}^{-1}$ . In a later work, a colorimetric sensor was developed based on a polymer fibre functionalized by a porphyrin molecule (CTAPP-PANAF) [13]. The functionalized fibre showed a significant color change when exposed to mercury ion samples, with sensitivity better than that of the  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  system; furthermore, the developed sensor can be used directly for the analysis of aqueous samples, without using any other organic solvent. Despite the good sensing performance, the CTAPP-PANAF system shows

however two great critical issues: the used materials are expensive, and the detection limit, although low, is not sufficient to detect quantities below the legal limit value allowed in drinking water by WHO ( $[\text{Hg}^{2+}]_{\text{max}} \approx 3 \times 10^{-8} \text{ M}$ ).

In this work we propose the use of the Colour Catcher® (CC) as a low-cost solid support with a proper optical set-up that allows reaching the sensitivity necessary for the trace detection of mercury ions together with an excellent selectivity versus other heavy metal cations.

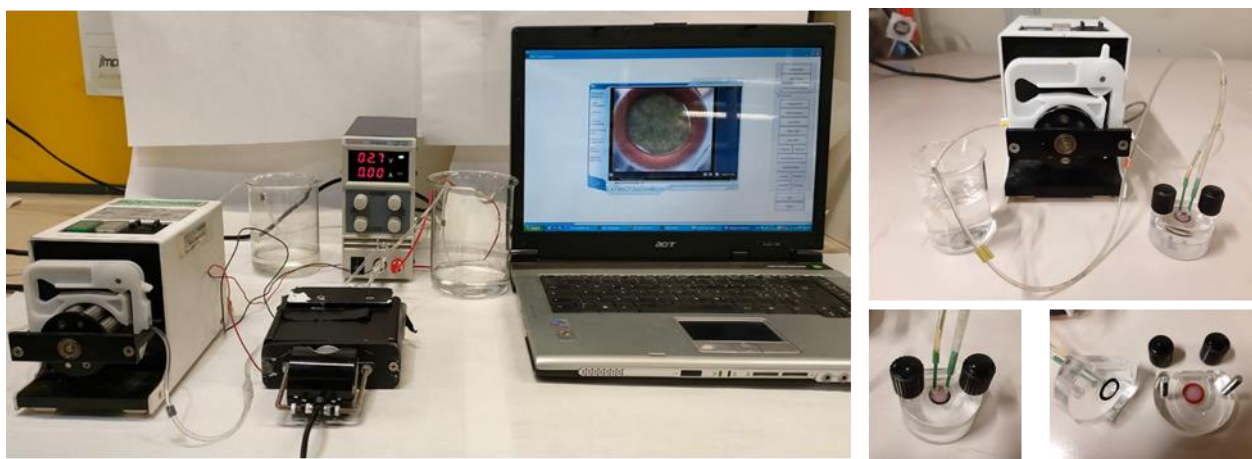
## Material and Methods

### Materials

**TCPPH<sub>2</sub> (P\*)** was synthesized in accordance to the literature [15], **HgCl<sub>2</sub>** (Sigma Aldrich) was commercially available and used as received. Colour Catcher® (CC), distributed in Italy by Grey (partner of the Henkel Company) and in England by Dylon, was bought in an Italian supermarket.

### Apparatus

UV-Vis spectra were performed with a Cary 100. A white LED was connected to bench power supply Eventek KPS3010D (0-30 V; 0-10 A). A digital camera Philips SPC900NC for notebook with a resolution of 352×288 pixels was used for recording the optical response. In flow measurement, a peristaltic pump PBI –international MS-Reglo was used, setting the flow rate at 6.5 mL/min.



**Figure 1** The optical setup used for measurements (webcam, LED, homemade holder, PC, bench power supply, peristaltic pump). On the right, the homemade holder in open and close configuration, where is inserted a CC@TCPH<sub>2</sub> strip cut in circular shape.

### Preparation of the CC@TCPH<sub>2</sub> sensor

**TCPPH<sub>2</sub> (P\*)** (0.708 mmol, 0.560 g) was dissolved in water (90 mL) and NaOH (0.1 M, 10 mL) was added in one portion. The mixture was stirred overnight at room temperature and the obtained solution was diluted 1:5 to achieve the final porphyrin concentration of  $1.45 \times 10^{-3} \text{ M}$ . A CC sheet of 35 cm<sup>2</sup> was dipped into the porphyrin solution for 5 minutes and then dried on a plate heated at 50 °C. The obtained CC@TCPH<sub>2</sub> sheet was washed with water and dried at 50 °C for three consecutive times to remove the porphyrin excess. The amount of porphyrin loaded onto the CC sheet (0.13 mg/cm<sup>2</sup>) was calculated by UV-visible spectroscopy by measuring the porphyrin concentration (after the 1:1250 dilution) before and after the immersion of the CC into the porphyrin solution.

### Optical measurements

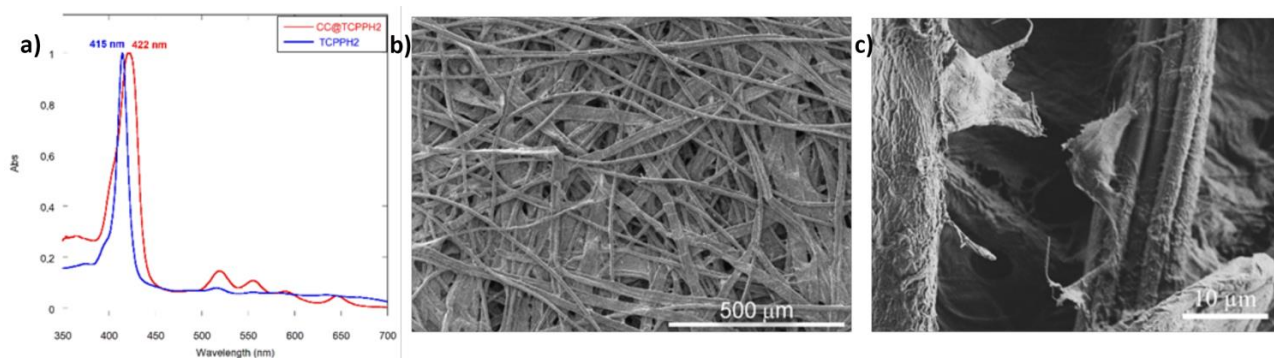
Individual solutions of  $\text{Hg}^{2+}$  were prepared dissolving the proper amount of  $\text{HgCl}_2$  in 2 L of distilled water to obtain mercury ions in the  $1.0 \times 10^{-8} - 1.0 \times 10^{-4}$  M concentration range. In all the samples the pH value was monitored before each measurement and adjusted at neutral pH by HCl or NaOH. In case of spectroscopic measurements, **CC@TCPPH<sub>2</sub>** was cut in a rectangular shape and inserted in a standard 1 cm cuvette containing the solution to be tested. For the colorimetric sensor set-up, the **CC@TCPPH<sub>2</sub>** sensor was cut in a circular shape, with a diameter of about 0.6 cm and then inserted in a homemade transparent polymethyl methacrylate (PMMA) holder fitted with a rubber O-ring as a gasket to prevent leakage (Figure 1). The holder has inlet and outlet connectors to allow the solution fluxes and interacts with the indicator. The flow was regulated by a peristaltic pump at the fixed rate of 6 mL/min. The water samples were made fluxed one-way through the measurement chamber without recirculation to prevent contamination or changes in the  $\text{Hg}^{2+}$  concentration of solutions. A commercial white LED served as excitation light sources, and a digital webcam was utilized to record the indicator scene. Illumination power stability has been tested by recording 12 hours baseline under distilled water flow. The measurement cell was closed in a black box that shields the sensor scene from ambient illumination. Before each measurement, indicators were conditioned for 5 minutes by fluxing distilled water. The signal from camera was acquired and elaborated by in-house Matlab codes.

## Results and Discussions

The CC is made up of strips of natural or artificial fabric (non-woven fabric), usually pressed between two steel cylinders [16] and it is generally used to absorb any leached colors in the wash avoiding clothes color changes. In general, the CC sheets are able to absorb the most common tissue dyes since they are made of polymer functionalized with positively charged groups (cationic polymer) [17] that act as electrostatic traps for negatively charged tissue dyes. In the literature few examples are reported about the use of CC as solid support for commercial anionic dyes [18]. These functionalized strips have been employed to detect metal ions or sulphides and thiols in liquid phase, but also in colorimetric gas sensor array to identify the degradation process of different meat and fish foods [19,20]. Since water-soluble indicators are easily absorbed in the CC, in this work we decided to deposit onto the CC sheets a water soluble and negatively charged tetrakis(4-carboxyphenyl) porphyrin, **TCPPH<sub>2</sub> (P\*)** by following a novel protocol, with the aim to detect mercury ions in aqueous solutions.

### CC@TCPPH<sub>2</sub> characterization

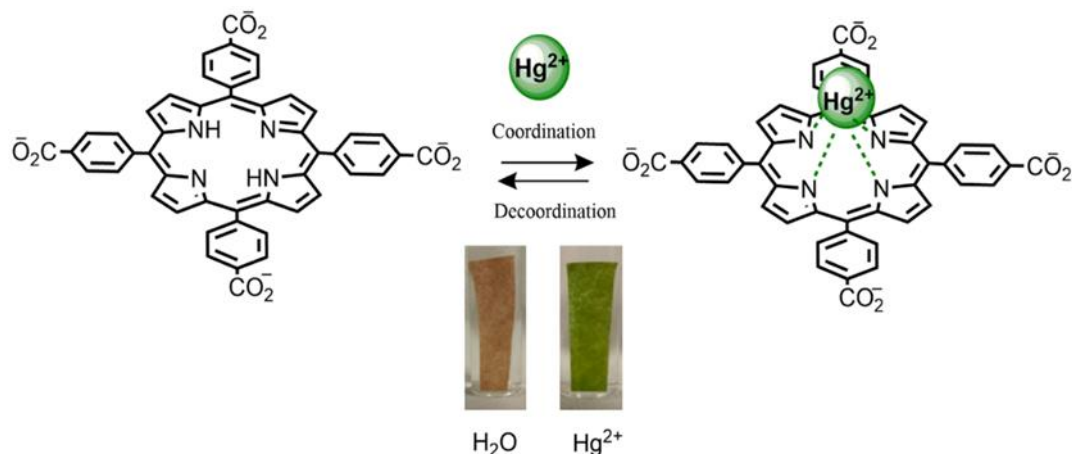
Remarkably, the absorbance spectra in the UV-Vis region was recorded in the linear range of the instrument by simply immersing the CC strip into a cuvette filled with water. Thereby, the spectroscopic technique can be utilized to investigate the properties of porphyrin films coating onto the CC. In distilled water, the functionalized CC strip preserves the characteristic spectral profile of porphyrin, showing well resolved Soret and four Q bands, red-shifted of around 7 nm with respect to those showed by **TCPPH<sub>2</sub> (P\*)** in water solutions (Figure 2a), suggesting that no strong porphyrin aggregation occurs onto the fibres. Furthermore, the spectra did not change within weeks, ruling out the occurrence of porphyrins leakage from the CC into solution over the time. The SEM images of **CC@TCPPH<sub>2</sub>** sample confirmed the high porosity of this polymeric material (Figure 2b and c), which consists of a very dense and homogeneous texture of fibres, making CC extremely effective for the uniform absorption of the water soluble receptor.



**Figure 2** a) UV-Vis spectra of  $\text{TCPPH}_2$  and  $\text{CC@TCPPH}_2$  in distilled water. b) and c) SEM characterization of the  $\text{TCPPH}_2$  ( $\text{P}^*$ ) functionalized Colour Catcher® surface.

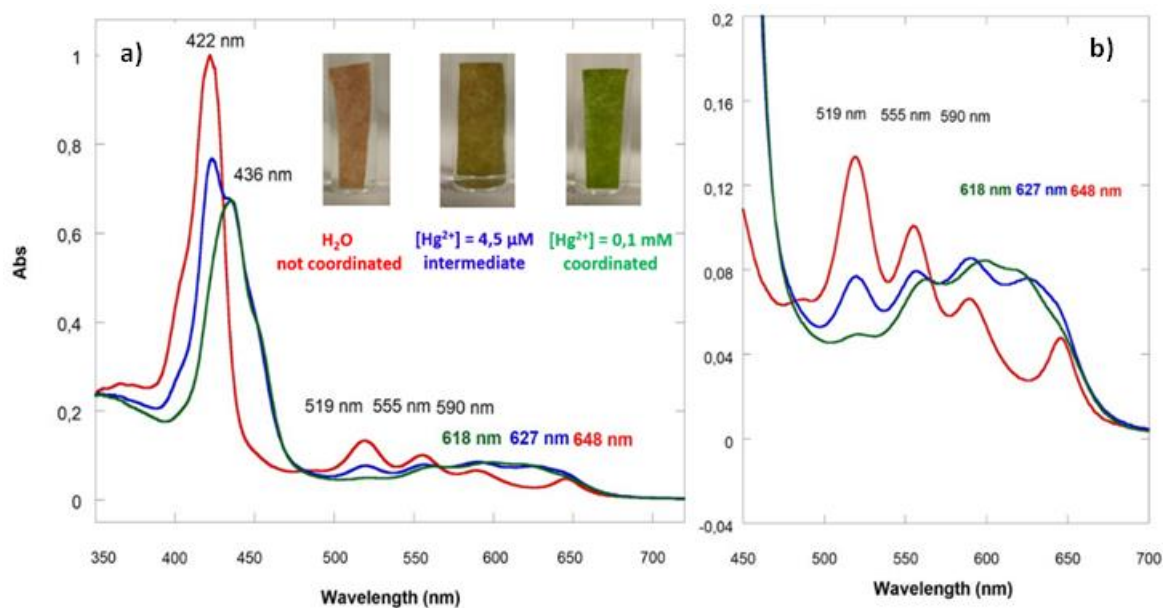
### UV-Vis mercury detection by $\text{CC@TCPPH}_2$

In presence of mercury ions,  $\text{CC@TCPPH}_2$  showed a clear colorimetric variation from dark pink to dark green observable to the naked eye (Figure 3).



**Figure 3.** The reversible coordination of mercury ion in the central core of the  $\text{TCPPH}_2$ . Below, the colorimetric variation of  $\text{CC@TCPPH}_2$  caused by the mercury coordination, from dark pink (non-coordinated species) to bright green (coordinated species)

The UV-Vis spectroscopy allowed us to detect the spectral changes and investigate the interaction mechanism ongoing directly on the solid-state sensor. Different CC strips, cut with the shape and size of a cuvette, were dipped in  $\text{HgCl}_2$  solutions of increasing concentrations. Figure 4 reports the UV-Vis profiles of  $\text{CC@TCPPH}_2$  after one hour from the immersion in solutions at different  $\text{Hg(II)}$  ion molarities. At higher concentrations, the porphyrins immobilized into the CC started to gradually coordinate the mercury ions, as evidenced by a clear color change to dark green. The UV-Vis profile presented a 14 nm Soret band shift (Figure 4a, green trace), accompanied by broadening of the Q bands (Figure 4b, green trace). These changes can be ascribable to the formation of the sitting-atop complex [10], where the ion is not completely inserted into the tetrapyrrolic core (Figure 3). At an intermediate concentration ( $[\text{Hg}^{2+}] = 4,5 \mu\text{M}$ ), the UV-Vis spectra evidenced an intermediate profile between the coordinated and uncoordinated forms and an intermediate color between dark pink and green.

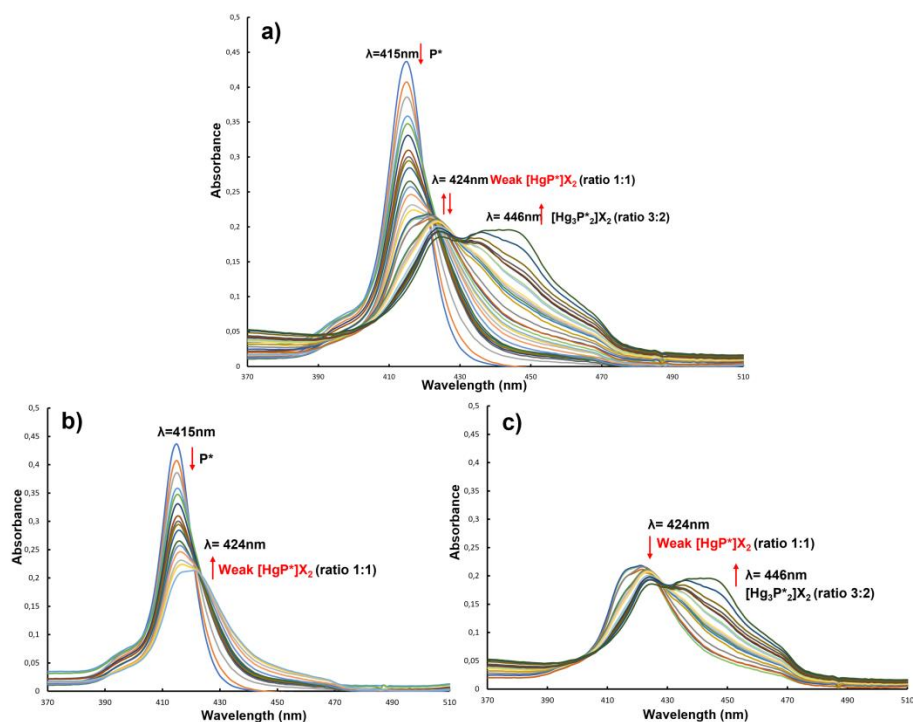


**Figure 4** a) UV-Vis spectral variations of **CC@TCPPH<sub>2</sub>** after one hour from the immersion in different solutions: water (red, not coordinated species), **HgCl<sub>2</sub>** 4,5  $\mu\text{M}$  (blue, intermediate species) and 0,1 mM (green, coordinated species). b) Magnification of Q bands region.

To have further insights supporting the proposed interaction mechanism, we studied by UV-Visible spectroscopy the interaction between **TCPPH<sub>2</sub>** (**P\***) and **HgCl<sub>2</sub>** in water solution. It is well known that mercury ions react with porphyrins by forming out-of-plane complexes showing different  $\text{Hg}^{2+}$ /porphyrin ratios. For example, it is reported that the formation of **HgP**, **Hg<sub>2</sub>P<sub>2</sub>** ( $\text{Hg}^{2+}$ /porphyrin = 1:1) and **Hg<sub>3</sub>P<sub>2</sub>** ( $\text{Hg}^{2+}$ /porphyrin = 3:2) complexes is strongly dependent on the porphyrin concentration [21]. According to these assumptions, the titration of **TCPPH<sub>2</sub>** (**P\***) with **HgCl<sub>2</sub>** was performed at different porphyrin concentrations. As reported in Figure 5a, at low concentration ( $2 \times 10^{-7}$  M of **TCPPH<sub>2</sub>**) **HgCl<sub>2</sub>** reacted with the free porphyrin **P\*** by forming two different species. Firstly, the decrease of the **P\*** adsorption (415 nm) was observed together with the raising of a new one at 424 nm (Figure 5b) [22] which, based on literature, was attributed to  $[\text{HgP}^*]\text{X}_2$  ( $\text{X} = \text{Cl}$  or  $\text{OH}$ ), the sitting-atop complex [21]. The observation of the isosbestic point at 419 nm revealed the direct transformation of **P\*** into the  $[\text{HgP}^*]\text{X}_2$  species. Then, the further addition of **HgCl<sub>2</sub>** to the reaction mixture (Figure 5c), was responsible for the direct transformation, as proved by the presence of the isosbestic point at 431 nm, of the  $[\text{HgP}^*]\text{X}_2$  into  $[\text{Hg}_3\text{P}^*_2]\text{X}_2$  that show the maximum of adsorption at 441 nm.

It should be noted that at higher **P\*** concentrations ( $2 \times 10^{-5}$  M of **TCPPH<sub>2</sub>**), the formation of  $[\text{HgP}^*]\text{X}_2$  was not observed and the complex  $[\text{Hg}_3\text{P}^*_2]\text{X}_2$  was the only species present in the reaction medium (Figure S1). In addition, by working at high porphyrin concentration some aggregation process can also occur, as revealed by the presence of broad adsorption bands in the UV-Vis spectrum.

Spectral changes observed when **CC** was reacted with **HgCl<sub>2</sub>**, resemble the process reported in Figure 5b which is associated to the establishment of weak  $\text{Hg}^{2+}$ /porphyrin interactions due to low porphyrin concentrations. Together with the well resolved peaks reported in Figure 4, this is a further evidence of the low aggregative state of porphyrins onto the **CC** that in turn was supposed to promote the weak 1:1 ratio  $\text{Hg}^{2+}$ /porphyrin interaction, as similarly described above for the formation of  $[\text{HgP}^*]\text{X}_2$  species in water solution.

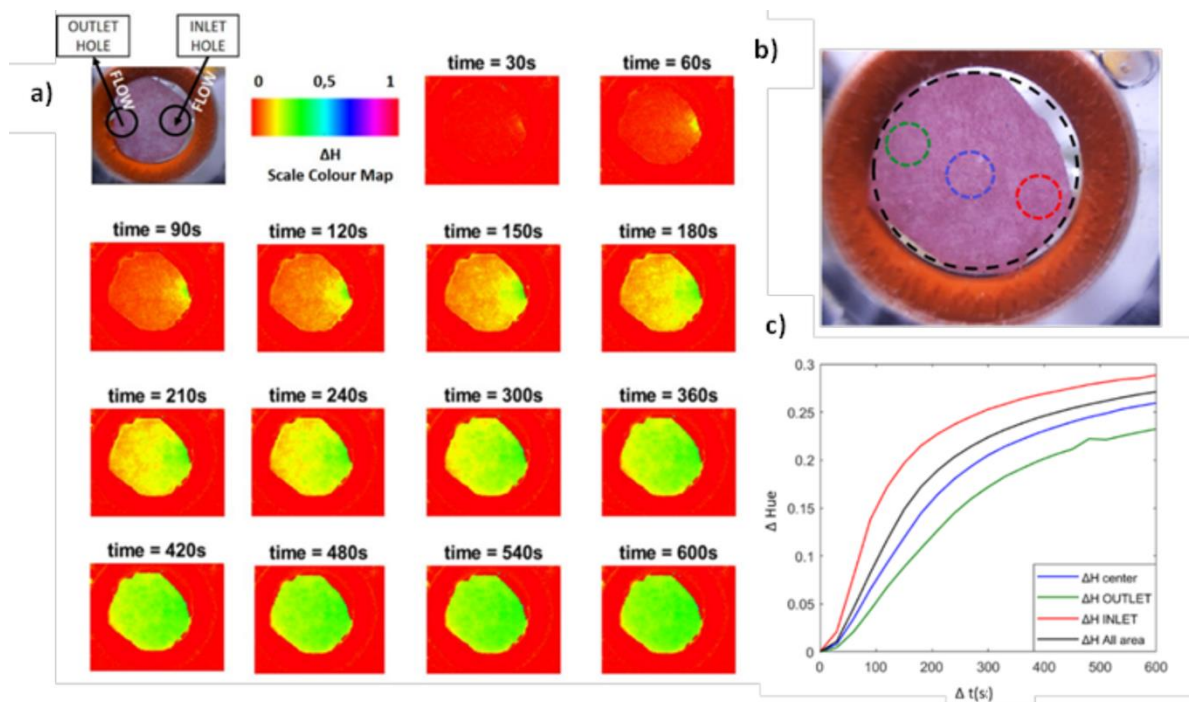


**Figure 5** a) Titration of  $\text{TCPPh}_2$  ( $\text{P}^*$ ) ( $2 \times 10^{-7}$  M) with  $\text{HgCl}_2$  in water under diluted conditions, b) decrease of the  $\text{P}^*$  adsorption at 415 nm and c) transformation of the  $[\text{HgP}^*]\text{X}_2$  into  $[\text{Hg}_3\text{P}^*_2]\text{X}_2$

### Colorimetric Measurement by $\text{CC@TCPPh}_2$

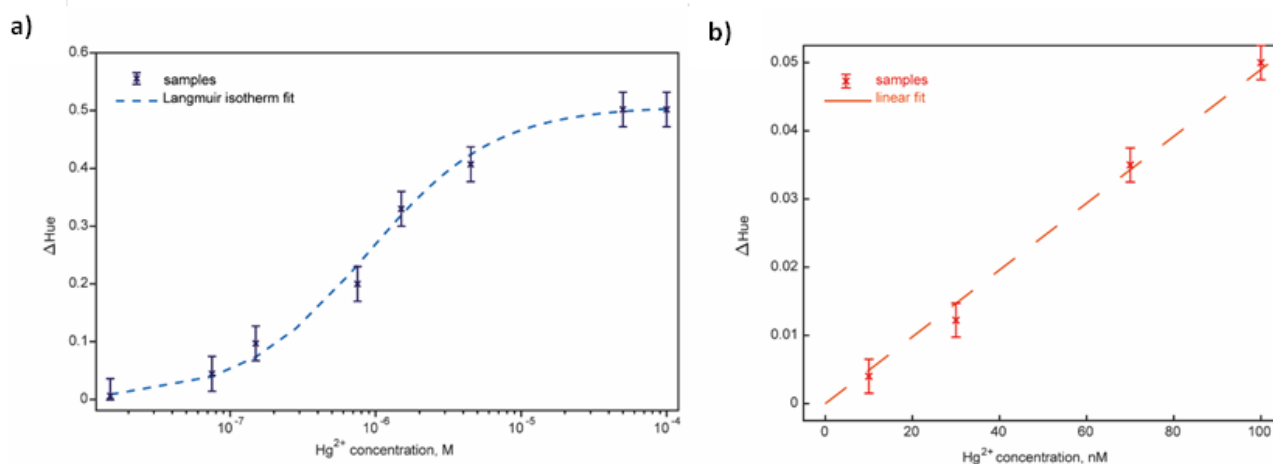
After assessing the interaction mechanism by spectroscopic measurements, colorimetric variations were recorded by a webcam keeping the  $\text{CC@TCPPh}_2$  under a constant sample flow. The acquired data were processed by a homemade software developed in Matlab, aimed at extracting the intensity of color variation occurring in a Region of Interest (ROI) utilizing the Hue as parameter. Hue belongs to the HSB (Hue Saturation Brightness) system, whose color space representation is based on human perception of a color. Here Hue degrees are normalized in [0,1] range and sensor response,  $\Delta\text{Hue}$ , has been considered as the variation from the initial Hue value. The use of this parameter greatly improves the stability of sensor response over background illumination changes, e.g. due to LED instabilities, since it correlates only with the color tone variation. Furthermore, RGB codification usually requires multivariate regression curves for the estimation of analyte concentrations. On the contrary, Hue compresses the information about color variation utilizing a single parameter, which makes easier the following sensor calibration. A second consideration concerns the use of a webcam as detector, which offers the possibility of averaging the indicator response over a large number of points, i.e. the pixels selected in the ROI. Averaging process attenuates the rms value of noise by a  $\sqrt{N}$  factor, where  $N$  in our case corresponds to ROI pixels that are approximately  $10^4$ . Despite the choice of low-resolution video, we found that the rms value of noise is lower than 0.001.





**Figure 6** Temporal evolution of the Hue through the representation of frames captured over the time during the flow measurements of a  $[\text{Hg}^{2+}] = 50 \mu\text{M}$  sample. On each image the value of Hue is represented according to scale of color map (left). Hue trend for each different ROI (Region of interest) integrated by the software: close to inlet hole (red), in the center (blue), close to outlet hole (green) and entire surface area (black).

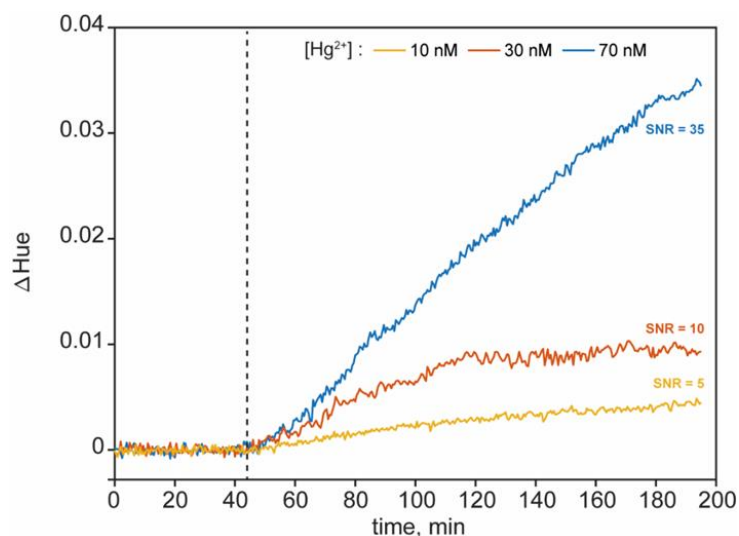
Figure 6 reports an example of the recorded response of the sensor scene when  $50 \mu\text{M}$  solution of  $\text{HgCl}_2$  was fluxed. The color maps report the Hue variation with respect to the initial value. From the image sequences it is possible observing the response of the membrane over the time, correlated with the flow direction as the result of the diffusion process of the analyte through the CC. The region of the CC closest to the inlet connector begins to respond (yellow and then green color in the map) and this variation is gradually spread all over the CC within 10 minutes. These images evidenced that the main limitation to time response is the lateral diffusion of the analyte in the membrane. Response time can be improved either by reducing the dimension of indicator disk, or by selecting a small ROI around to the inlet as confirmed, for example, by red dashed circle and corresponding response trend in Figure 6b and 6c. To avoid alterations due to changes in the relative proximity from the inlet hole during the different measurements, hereinafter results are referred to the response associated to the whole indicator area (black circle in the Figure 6b). The integration on the entire membrane surface therefore caused the loss of optical information about the short response times but allowed to strongly decrease the noise of the device, since it processed several interaction sites on the entire sensor surface. Thus, it was possible to decide whether to integrate only in the area close to flow inlet hole, if interested about a quickly answer despite an increase of device noise, or whether to integrate the entire membrane area, if interested about the long-term response allowing to drastically reduce the device noise. In conclusion, the porphyrin quickly coordinated the mercury ions turning green in the nearby of inlet hole; the remaining response time was due to the diffusion of the analyte trough the porous CC medium. The porosity of the polymer fibres, confirmed by SEM images (Figure 2), allowed the analyte to easily spread across the entire membrane and to come rapidly into contact with the deposited receptor.



**Figure 7** a) Langmuir isotherm fit of  $\Delta H$  value recorded at equilibrium condition, after 6 hours of sample flow, as a function of logarithm of  $[\text{Hg}^{2+}]$  concentrations in the range [10 nM-0,1 mM]. b) Linear fit in the concentration range  $[\text{Hg}^{2+}] = [10 \text{ nm}-1\mu\text{M}]$ .

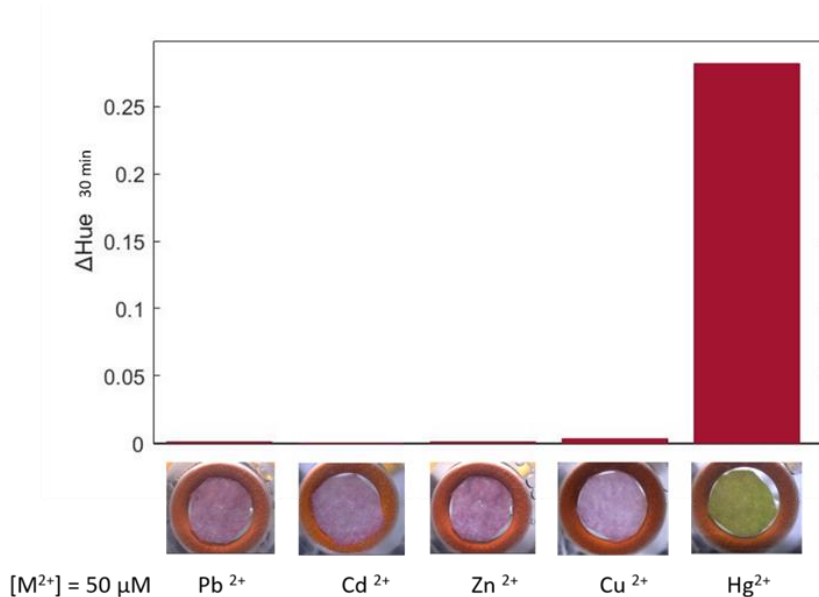
Figure S3 shows the temporal evolution of  $\Delta\text{Hue}$  value. The saturation maximum value of the final colorimetric variation was proportional to the metal ion concentration that interacted with the macrocycle core. Calibration curves were performed at increasing  $\text{HgCl}_2$  concentrations in 10 nM to 0.1 mM range, recording the final saturation maximum value of  $\Delta\text{Hue}$  observed after 6 hours. Using semilogarithmic scale (Figure 7a), responses follow a sigmoid trend with the mercury concentration in solution. Considering the overall interval, data can be fitted by Langmuir isotherm observing a good capability to explain the color changes over  $\text{Hg}^{2+}$  concentration ( $R^2 = 0.9806$ ) and relatively low RMSEC (root mean square error in calibration).

Since legal limit of mercury in drinking water is equal to  $6 \mu\text{g/L}$  ( $[\text{Hg}^{2+}]_{\text{max}} \approx 3 \times 10^{-8} \text{ mol L}^{-1}$ ) [6], colorimetric measurements around this concentration were performed to test the system performance for applications in real field conditions (Figure 7b and Figure 8). Calibration showed a good linearity at low concentration (Figure 7b) confirming the possibility to utilize the proposed approach in applicative contexts. Furthermore, response signal was significant for analytical purposes at  $[\text{Hg}^{2+}] = 10 \text{ nM}$ , three times below mercury legal limit in water.



**Figure 8** Optical responses in terms of Hue for  $[\text{Hg}^{2+}] = 10 \text{ nM}$  (yellow line), 30 nM (orange line) and 70 nM (blue line)

Finally, considering that the sensor selectivity is a further parameter to be considered, the **CC@TCPPH<sub>2</sub>** sensor response was tested in presence of four other metal ions: Zn<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>. In this regard, optical measurements were made for independent solutions of each metal ion at a concentration of 50 μM, which corresponds to a concentration above the legal limit of all these metal ions in drinking water, as established by WHO [6,23]. The Hue response negligibly changed after 1h from the immersion into contaminated water samples. On the other hand, at the same concentration mercury produced a dramatic color change to dark green after few minutes, leading to a sharp increase of the Hue value. The comparison between Hue values recorded after 1 hour confirmed the great selectivity of the sensor for mercury (see Figure 9), excluding any colorimetric alteration due to the presence of other possible interfering metal ions in the real water samples. The outcomes confirmed that the investigated sensing approach is a viable solution for real-world mercury detection, further considering the extremely low sensitivity to the other metal ions that can generally occur in water samples.



**Figure 9** Comparison of  $\Delta$  Hue values recorded after 60 minutes of measurement in independent solutions of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup> at the concentration of 50 μM.

## Conclusions

The instrumental setup of the **CC@TCPPH<sub>2</sub>** sensor showed an excellent sensitivity, able to detect even small traces of mercury in aqueous samples (up to  $1 \times 10^{-8}$  M), below the limit value legally allowed in drinking water [6]. This is a very good achievement, since, to the authors best knowledge, previously reported colorimetric sensors did not show a sensitivity sufficient to detect such small amounts of mercury [12,13]. The response times were extremely short for concentrations in the  $10^{-6}$ - $10^{-5}$  M range; in the first 15 minutes a signal was clearly distinguishable from the noise, making the system a suitable device for real-time analysis of water resources. The sensor showed a great selectivity for the mercury and was able to preserve the measurement from the matrix effect by possible contaminants in real water analysis. All these properties make the **CC@TCPPH<sub>2</sub>** perfectly suited to *in situ* monitoring of natural water sources or industrial discharges. This work paves the way for the future development of sensors array using the CC as a common and versatile solid support for a wide range of receptors. An array that uses receptors of different nature, each one with

a different selectivity to the various analytes present in a complex matrix as sample, can be able to perform a complete analysis about matrix composition.

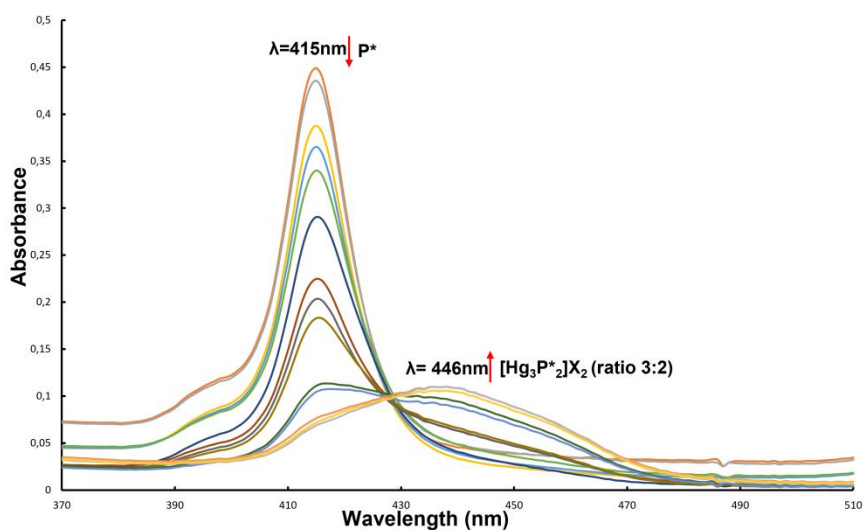
## References

- 1) a) H. Ed. Bradl, *Heavy Metals in the Environment: Origin, Interaction and Remediation, 1st ed., Interface Science and Technology*, 2005, 6. b) D. A. Wright, P. Welbourn, *Environmental Toxicology, Cambridge University Press: New York*, 2002.
- 2) a) B. A. Fowler, M. Nordberg, L. Friberg, G. Eds. Nordberg, *Handbook on the Toxicology of Metals, 3rd ed., Academic Press: Boston*, 2007. b) L. Br. Jaerup, Hazards of heavy metal contamination, *Med. Bul.*, 2003, 68, 167–182. doi: 10.1093/bmb/ldg032
- 3) M. Balali-Mood, K. Naseri, Z. Tahergorabi, MR. Khazdair, M. Sadeghi, Toxic Mechanisms of Five Heavy Metals: Mercury, Lead, Chromium, Cadmium, and Arsenic, *Front. Pharmacol.*, 2021, 12, 643972. doi: 10.3389/fphar.2021.643972
- 4) R.A. Bernhoft, Mercury toxicity and treatment: a review of the literature. *J Environ Public Health.*, 2012, 2012, 460508. doi: 10.1155/2012/460508.
- 5) P.B. Tchounwou, C.G. Yedjou, A.K. Patlolla, D.J. Sutton, Heavy metal toxicity and the environment, *Experientia supplementum*, 2012, 101, 133–164. doi: 10.1007/978-3-7643-8340-4\_6
- 6) World Health Organization's (WHO) Guidelines for drinking-water quality 4<sup>th</sup> edition, 2017, 631.
- 7) J.R. Askim, M. Mahmoudi, S.K. Suslick, Optical sensor arrays for chemical sensing: the optoelectronic nose *Chem. Soc. Rev.*, 2013, 42, 8649-8682. doi: 10.1039/C3CS60179J
- 8) Z.Wang, M. A. Palacios, P. Anzenbacher, Jr., *Anal. Chem.*, 2008, 80, 7451–7459. doi: 10.1021/ac801165v
- 9) L. Capitan-Valley, N. Lopez-Ruiz, A. Martinez-Olmos, M. Erenas, A. Palma, Recent developments in computer vision-based analytical chemistry: A tutorial review *Anal. Chim. Acta*, 2015, 899, 23-56. doi: 10.1016/j.aca.2015.10.009
- 10) R. Paolesse, S. Nardis, D. Monti, M. Stefanelli, C. Di Natale Porphyrinoids for Chemical Sensor Applications *Chemical Reviews*, 2017, 117 (4), 2517-2583. doi: 10.1021/acs.chemrev.6b00361
- 11) K. Suslick, N. Rakow, A colorimetric sensor array for odour visualization, *Nature*, 2000, 406, 710–712. doi: 10.1038/35021028
- 12) D. Filippini, A. Alimelli, C. Di Natale, R. Paolesse, A. D'Amico, I. Lundström, *Chemical sensing with familiar devices, Angew Chem. Int. Ed.*, 2006, 45, 3800–3803. doi: 10.1002/anie.200600050
- 13) L. Xiaoxing , L. Xiaojuan ,T. Minli, Z. Wenqin, A highly selective and sensitive recyclable colorimetric Hg<sup>2+</sup>-sensor based on the porphyrin-functionalized polyacrylonitrile fiber *J. Mater. Chem. A*, 2015, 3, 13254-13262 doi: 10.1039/C5TA02491A
- 14) S. Lei, L. Yaoxian, S. Mingda , W. Hengguo , X. Shufei , Z. Chaoqun , Y. Qingbiao, Porphyrin-functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core/shell magnetic colorimetric material for detection, adsorption and removal of Hg<sup>2+</sup> in aqueous solution *New J. Chem.*, 2011, 35, 2697-2704. doi: 10.1039/C1NJ20307J
- 15) L. Carlucci, G. Ciani, S. Maggini, D. M. Proserpio, F. Ragaini, E. Gallo, M. Ranocchiarri and A. Caselli, Synthesis and characterization of new tetra-substituted porphyrins with exo-donor carboxylic groups as building blocks for supramolecular architectures: Catalytic and structural studies of their metalated derivatives *J. Porphyrins Phthalocyanines* 2010, 14, 804-814 doi: 10.1142/S1088424610002641
- 16) M. Luoni, G. Li Bassi, «Non-woven Colour-Catcher fabric and method for its preparation » (U.S Patent No. US2009/0137170 A1), 2009
- 17) I. Tabujew, K. Peneva, Functionalization of Cationic Polymers for Drug Delivery Applications, in *RSC Polymer Chemistry in Regenerative Medicine*, 2015, 1-29.
- 18) G. Alberti, V. M. Nurchi, L. R. Magnaghi, R. Biesuz, A portable, disposable, and low-cost optode for sulphide and thiol detection *Anal. Methods*, 2019, 11, 4464-4470 doi: 10.1039/C9AY01538H
- 19) L. R. Magnaghi, G. Alberti, F. Capone, C. Zanon, B. Mannucci, P. Quadrelli, R. Biesuz, Development of a Dye-Based Device to Assess the Poultry Meat Spoilage. Part II: Array on Act *J. Agric. Food Chem.*, 2020, 68, 12710-12718 doi: 10.1021/acs.jafc.0c03771
- 20) L.R. Magnaghi, F. Capone, C. Zanon, G. Alberti, P. Quadrelli, R. Biesuz, Colorimetric Sensor Array for Monitoring, Modelling and Comparing Spoilage Processes of Different Meat and Fish Foods *Foods*, 2020, 9, 684 doi: 10.3390/foods9050684
- 21) a) Z. Valicsek, G. Lendvay, O. Horvat, Equilibrium, Photophysical, Photochemical, and Quantum Chemical Examination of Anionic Mercury(II) Mono- and Bisporphyrins *J. Phys. Chem. B*, 2008, 112, 14509 doi: 10.1021/jp804039s; b) O. Horvat, Z. Valicsek, A. Vogler, Unique photoreactivity of mercury(II) 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin *Inorg. Chem. Commun.*, 2004, 7, 854-857 doi: 10.1016/j.inoche.2004.05.004; c) O. Horvat, R. Huszank, Z. Valicsek, G. Lendvay, Photophysics and

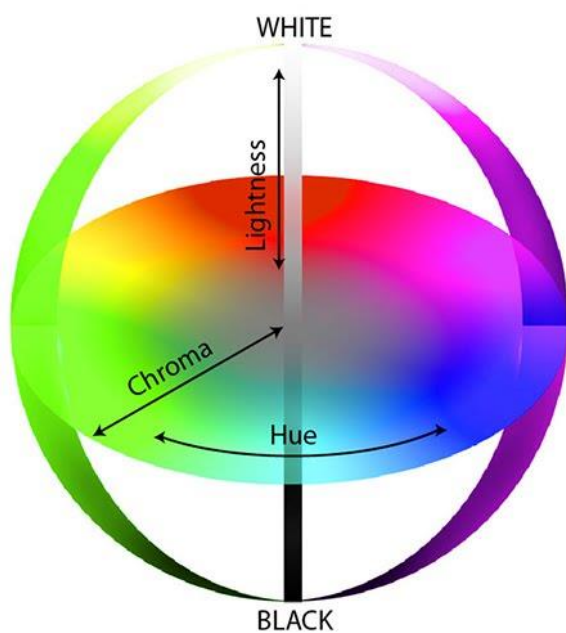
photochemistry of kinetically labile, water-soluble porphyrin complexes *Coord. Chem. Rev.*, 2006, 250, 1792  
doi.org/10.1016/j.ccr.2006.02.014

- 22) A. O. Adeyemo, M. Krishnamurthy, Equilibrium studies on mercury(II)—porphyrins in aqueous solution *Inorg. Chim. Acta*, 1984, 83, L41-L43 doi: 10.1016/S0020-1693(00)82504-9
- 23) Background document for preparation of WHO Guidelines for drinking-water quality. Geneva, World Health Organization, 2003, (WHO/SDE/WSH/03.04/88).

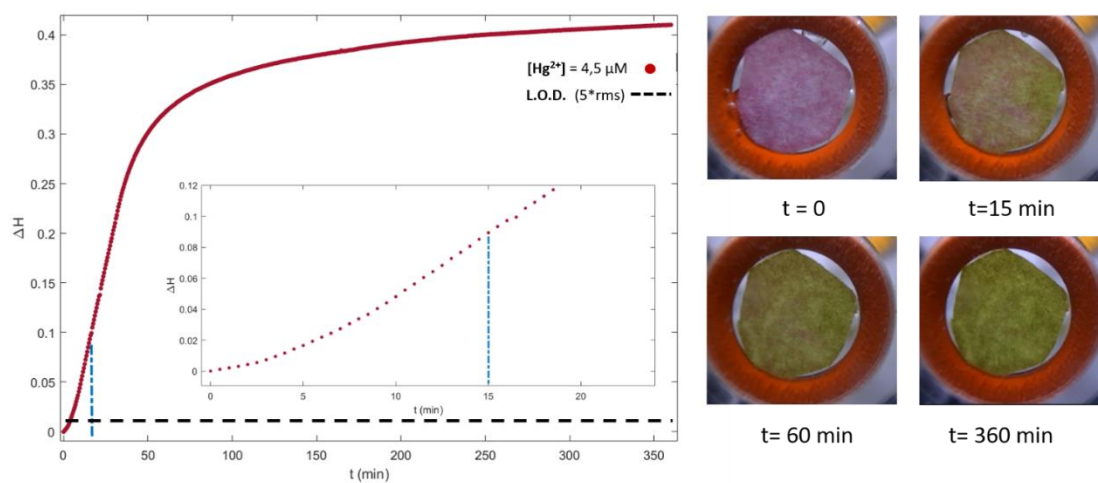
### Supporting Information



**Figure S1:** Titration of TCPPH<sub>2</sub> (P\*) ( $2 \times 10^{-5}$  M) with HgCl<sub>2</sub> in water under concentrated conditions.



**Figure S2** Color representation system HSB (Hue, Saturation, Brightness).



**Figure S3** Variation of the  $\Delta H$  parameter during flow optical measurement of the  $[\text{Hg}^{2+}] = 4,5 \mu\text{M}$  solution(left). Photos captured by the web cam from the optical measurement video at different time intervals (right).