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Fast Optical Sensing of Metals: A Case Study of Cu²⁺ Assessment in Soils

Larisa Lvova,[1,z] Elisa Acciari,[1] Federica Mandoj,[1] Giuseppe Pomarico,[2] and Roberto Paolesse[1,*,z]

¹Department of Chemical Sciences and Technology, University "Tor Vergata", Via della Ricerca Scientifica 1- 00133 Rome, Italy
²University of Brescia, Department of Molecular and Translational Medicine, Viale Europa, 11—25123 Brescia, Italy

In this paper we report an application of a novel porphyrin ligand, Zn(II)TPP-BPI-crown (ZnPC), functionalized with two dibenzo-crown-ether moieties as cation-sensitive ionophore. The test on the optical response of ZnPC ligand inside PVC-based polymeric membranes towards different cations (Na⁺, K⁺, Li⁺, Ca²⁺, Mg²⁺, Co²⁺, Cd²⁺, Pb²⁺, Zn²⁺, Cu²⁺ and NH₄⁺) were performed. The influence of the lipophilic site functionalization on the ZnPC optode response was investigated. The visibly (naked eye) observed color change of sensing material from green to red demonstrated the suitability of the ZnPC-based optodes to perform fast monitoring of Cu(II) ions in the concentration range between 6.6×10^{-7} and 2.4×10^{-2} mol l⁻¹, with a low detection limit (estimated by s/n = 3 method) of 0.03 mg l⁻¹, which is lower than WHO guideline value of 2 mg l⁻¹ for natural waters. The membranes with the best composition were deposited onto paper support and employed for the express analysis of copper(II) ion in aqueous soil extracts. The results obtained were in a good agreement with a standard ASS method, thus suggesting the utility of developed sensors for aims of express environmental monitoring.

Transition and heavy metal ions assessment is a topic of intense research, due to their strong impact on natural processes[1,2]; many of them are essential elements in plants, animals and humans, while others are toxic for environment and living beings.[3,4] Occurring both from anthropological and natural sources, these species are present in soil, water reservoirs and ocean environment,[5–7] and through accumulation in plants and animals, easily enter the human food-chain.[8–10]

Among transition metals, copper is one of the important essential trace elements, since it is a key constituent of enzyme complexes.[11] The copper deficiency in children can lead to anaemia, neutropenia and bone demineralization,[12] while in adults this effect is less evident, but low copper intakes may have adverse effects for individuals with Wilson disease.[13] On the contrary, taken in a large quantity copper becomes toxic, causing typical symptoms of food poisoning, such as nausea, vomiting, diarrhoea, etc., and may cause gastrointestinal bleeding, intravascular haemolysis, hepatocellular toxicity and acute renal failure.[14]

Copper is widely used in the electrical industry, in the production of alloys, in the textile industry and in the agriculture. Due to this wide distribution, copper is one of the main polluting species in the environment. The main source of copper uptake for humans is food (dietary). In the food chain copper arises principally from natural waters and plants, the copper content in which is related to the occurrence in soils, and hence, the levels of copper pollution in soils should be monitored.

Among the standard methods for the copper analysis, Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Atomic Emission Spectroscopy coupled Plasma Mass Spectrometry (ICP-MS) are the most commonly used techniques.[15] Even if their high precision is indisputable, standard analytical methods are time consuming, employ costly and sophisticated equipment, which requires the involvement of experienced personnel, and need a careful procedures for sample storage and pre-treatment prior to analysis. The application of chemical sensors and multisensory systems has found a lot of interest for environmental monitoring tasks, and for transition and heavy metal ions detection,

in particular due to the obvious advantages of simple preparation and handling, low cost, reasonable selectivity and improved sensitivity.[16–18]

The development of novel sensing materials with analytically useful sensitivity toward metal cations for application in optical chemical sensors is nowadays a challenging task. Ionophores are key components that significantly contribute to the selectivity of polymeric membrane sensors. The use of compounds such as calix[n] arenes, crown-ethers, porphyrins or other ligands containing a cavity of determined size, has previously permitted to develop highly selective electrochemical sensors for cations.[19] Combined with optical transduction, chemical sensors doped with specific ligands give the possibility to perform fast visible analyses on the presence/absence and concentration of a target analyte. Recently, optical sensors for Cu²⁺ ions detection based on quantum dots with anchored ligands,[20] aza-macrocycles decorated metallic surfaces,[21] and polymers,[22] metallic and silicon nanoparticles,[23] and microspheres,[24] have been reported. However, despite the evident benefits, only few works on naked-eye visible detection of metal cations have been published.[25–29]

Among different macrocycles previously employed for Cu²⁺-selective optical sensors development, porphyrins represent a particular interest, due to their rich chemistry determined by delocalized aromatic π-system, specific optical (both UV–vis absorption and emission bands) and electrochemical properties and the possibility to be employed in chemical sensors with different transduction principles (electrochemical, optical, multi-transduction, etc.).[30–32] Nevertheless, less progresses were achieved in the development of porphyrin-based cation-selective optodes, the response of which is dependent on ionophore-analyte interaction and luminescence variation upon complexation.[33]

Recently we have reported the synthetic procedure for the preparation of Zn-complex of tetraphenylporphyrin-1,3-bis(2-pyridylimino)isoindoline conjugate, ZnTPP-BPI, and its application for selective fluorescence sensing of Pb²⁺ ions in solution,[34] In the present work we have continued our investigations on development of optical sensors for environmental monitoring,[35–37] and reporting the use of a novel porphyrin ligand, Zn(II)TPP-BPI-crown (ZnPC) (Fig. 1), functionalized with two dibenzo-crown-ether moieties as cation-sensitive ionophore for fast optical assessment of metal

*Electrochemical Society Member.
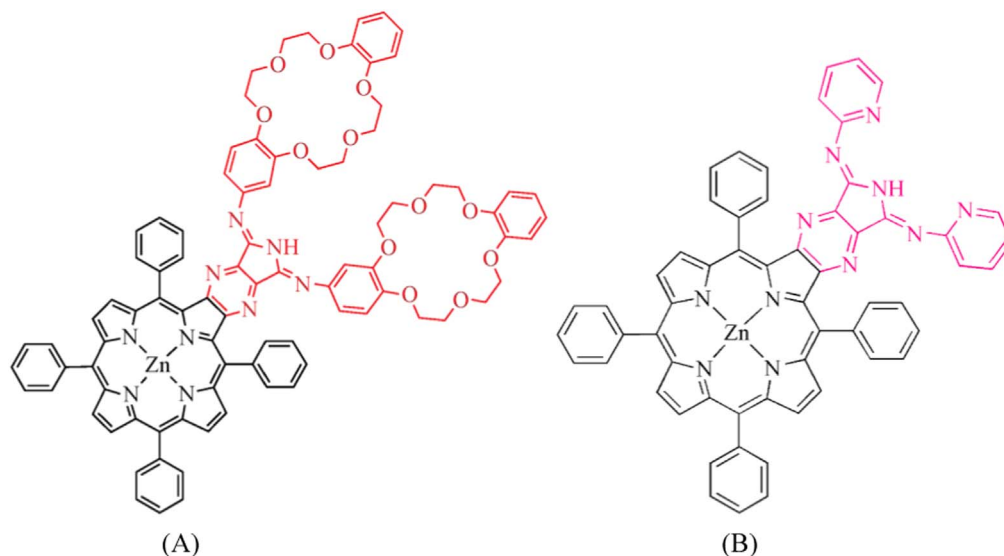ᶻE-mail: larisa.lvova@uniroma2.it; roberto.paolesse@uniroma2.it

Figure 1. Chemical structures of the tested ligands: (A) ZnPC and (B) ZnTPP-BPI.

cations. The fluorescence properties of ZnPC ligand were studied first in solution, then inside PVC-plasticized polymeric membranes. The influence of different concentrations of cation-exchanger, potassium tetrakis-(4-chlorophenyl)borate (TpClPBK), on the selective properties of developed optical sensor was investigated. The disposable sensors, both on glass and paper support, supplemented with familiar devices for signal acquisition (LED as light source and a digital camera as a signal detector), or working on a naked-eye mode were developed. The visibly observed color change of sensing material from green to red demonstrated the suitability of the ZnPC-based optodes to perform fast monitoring of Cu(II) ions in soils extracts in the wide concentration range.

Experimental

Reagents.—The Zinc[5,10,15,20-Tetraphenylporphyrinato-2,3-(1′,3′-bis(imino-dibenzo-18-crown-6))], ZnPC, and tetraphenylporphyrin-1,3-bis(2-pyridylimino)isoindoline, ZnTPP-BPI, ligands were synthesized and completely characterized in our laboratories.[34,38] The chemical structures of tested ligands are shown in Fig. 1.

Polymeric membranes preparation and optodes testing.—Polymeric membrane components, such as high molecular weight poly(vinyl cloride) (PVC), tris(2-ethylhexyl) phosphate (TOP) plasticiser, potassium tetrakis-(4-chlorophenyl)-borate (TpClPBK) employed as a cation-exchanger were purchased from Fluka. 4-(2-Hydroxyethyl) piperazine-1-ethanesulfonic acid (HEPES), used to prepare a buffer background solution, and chlorides of the following cations: Na^+, K^+, Li^+, NH_4^+, Ca^{2+}, Mg^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, nitrates of Pb^{2+} and Zn^{2+} were purchased from Sigma-Aldrich and used directly without further purification. THF (Sigma-Aldrich) was freshly distilled prior to use. Ultrapure water was used for aqueous solution preparation.

Polymeric membranes were prepared by incorporation of 1 wt% of ionophore and 0.5–5 wt% of TpClPBK inside a polymeric matrix containing PVC and plasticizer in 1:2 ratio by weight. The membranes of total weight of about 100 mg, were dissolved in 1 ml of THF. In total 5 membranes of different compositions, namely membranes Mb1-Mb3 based on ZnPC ligand, and membranes Mb4-Mb5 based on ZnTPP-BPI, were prepared and tested, Table I. The membranes were cast onto a glass slide support (Brand GMBH, Germany, Cat.N 474743, 75 × 25 mm size) by drop casting method; in order to guarantee the replicated measurements, from 4 to 10 sensing membrane spots were deposited on the same support.
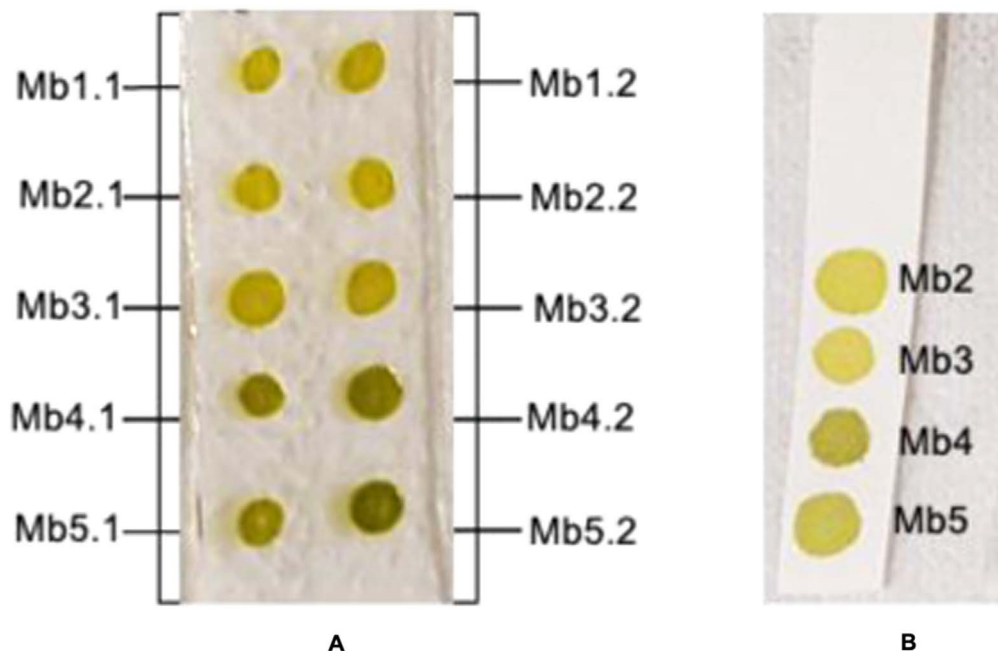
About 7–10 μl of every membrane cocktail were cast onto transparent glass slides (2.5 mm × 0.8 mm size), or paper support (Whatman 1003–110, 390 μm thickness, 185 g m^{-2}, filter paper strips cutted of 3.5 mm × 0.5 mm size), by drop casting method, Fig. 2. In order to guarantee the replicated measurements at least 2 sensing spots for every membrane were deposited on the same glass support. For on-paper based optodes at least three sensing spot areas (n = 3, d = 5 pixels) were extracted at the center of every single sensing spot. THF solvent was allowed to evaporate overnight, afterwords the "disposable" optode sensors were tested in individual solutions of several cations in $3.3 \times 10^{-7} - 2.2 \times 10^{-2}$ mol l^{-1} concentration range on 0.01 M HEPES pH 7.4 background. Metal salts stock solutions (1 mol l^{-1}) were prepared dissolving corresponding amounts of metal chlorides or Pb(II) and Zn(II) nitrates in distilled water, lower concentration solutions were obtained by consecutive additions of calculated amounts of corresponding stock solution.

Optical measurements.—Optical absorption spectra were reordered with an Agilent Cary 50 UV–vis spectrophotometer. A 9.4 μM ZnPC solution in THF was placed in a 10 mm path length glass cell of 3.5 ml volume and UV–vis spectra were recorded in wavelength diapason from 350 to 800 nm. Photoassisted Technique (PT) measurements were performed in polystyrene cuvettes (Katrell, model 1937) of 10 mm path length; the sensor output in the form of snapshots taken by digital or a smartphone was registered from a fixed distance and the color variations were analyzed in RGB space with respect to the three main visible spectrum colors: Red (630 nm), Green (530 nm), and Blue (480 nm). The video and image outputs were transferred into digital signals through application of in house written codes (Matlab, v. 9.2, 2017, The MathWorks, Inc., Natick, USA). The RGB values were extracted at the center of every single sensing spot (n = 3, d = 25 pixels) and evaluated subtracting the intensity of the sensing spot without the analyte and glass or paper background. In order to obtain calibration curve, the film optical intensity was plotted vs analyte concentration change.

Real samples analysis.—The developed optical sensors were tested both in a single sensor mode and inside a sensor array for fast optical assessment of Cu^{2+} in aqueous extracts of nine soil samples with different anthropological impact, Table II. Among them three samples were from waste dumps (Sample 1, 2 and Sample 5), samples 4 and 6 were topsoils from private gardens (Castelli Romani zone, Rome, Italy), sample 9 was taken in "Tor Vergata" University garden of Science Faculty (Sogene building, Tor Vergata zone of

Table I. The compositions of studied membranes.

Membrane	Ligand, 1 wt%	Plasticizer	TpClPBK, wt%
Mb1		TOP	0.5 wt%
Mb2	ZnPC	TOP	1 wt%
Mb3		TOP	5 wt%
Mb4	ZnTPP-BPI	TOP	0.5 wt%
Mb5		TOP	5 wt%

directly in the overlying over soil sample liquid phase, without sample filtration and separation. The sensor response was almost immediate with notable sensing spot color change from green to red.

The amount of Cu^{2+} ions in soil samples 1–5 was evaluated by standard Atomic Absorption Spectroscopy (AAS) method on Perkin Elmer Analyst 600 high performance optical system combined with a Transversely Heated Graphite Atomizer (THGA) furnace assembly. AAS was calibrated with standard solutions contained 1 mg ml^{-1} of Cu^{2+} (Carlo Erba, Italy) by 3 points calibration. The 324.8 nm wavelength was employed for Cu^{2+} optical detection.

Figure 2. (A) Schematic representation and image of glass slide with deposited replicated membranes Mb1-Mb5; (B) the photograph of paper strips with deposited Mb2, Mb3 and Mb4, Mb5 based on ZnPC and ZnTPP-BPI respectively.

Table II. Results of Cu^{2+} presence evaluation in aqueous extracts of soils with ZnPC doped membrane Mb3 (n = 3).

		[Cu^{2+}], mg kg^{-1}	
	Sample	AAS	Mb 3
1	Rubbish dump 1 (Ronciglione, site 1)	0.717	0.252 ± 0.071
2	Rubbish dump 2 (Borgo val di Taro)	0.338	0.212 ± 0.060
3	Ciampino Airport	46.9	43.6 ± 1.26
4	Private Garden 1	0.359	0.210 ± 0.066
5	Rubbish dump 3 (Ronciglione, site 2)	0.351	0.190 ± 0.062
6	Private Garden 2	—	0.210 ± 0.067
7	Gas Station 1	—	1.49 ± 0.158
8	Gas Station 2	—	1.11 ± 0.116
9	University Garden	—	8.53 ± 1.21

Rome, Italy); the last two samples (sample 7 and 8) were sampled in close proximity to gas stations situated in Tor Vergata zone of Rome, Italy. The raw soil samples (approximately 10–15 g weight) were handpicked from the surface of 0.5 m^2 in selected sites, mixed and sieved, afterwards 1 g amount of every sample was taken inside glass vessel and extracted with 5 ml in 0.01 M HEPES pH 7.4 solution for 24 h, except for sample 5 for which the quantities have been halved. After the formation of the two phases, the filtrate was separated from the solid soil phase, placed in transparent cuvette and Cu^{2+} content was tested with on glass-deposited optodes without any other pretreatment. On-paper sensing strips were employed

Results and Discussion

Following our previous research on the synthesis, characterization and application of ZnTPP-BPI as an effective chemosensor for detection of metal ions,[34] in the present work we have decided to modify one of the ligand binding centers (BPI unit in particular) with two dibenzo-crown-ether moieties, varying in such a way the system chelating properties and tuning selectivity towards cations of determined size. In the novel ZnPC ionophore the ZnTPP unit is expected to act as an optical signalling unit, while the two crown-ether moieties will serve as guest-binding site (or sites). A visible optical output of the sensor based on ZnPC ligand is expected through the interaction with analyte and will be determined by variation of porphyrin signaling unit.

We first have focused our attention on investigating copper ion-ZnPC interaction, since ZnPC-based optical sensors may be a promising system for Cu^{2+} detection. Copper amount environmental monitoring is extremely important because it can be a toxic pollutants that lead to different pathologies.[13] According to WHO recommendations, the permitted values for copper are 50–140 mg K^{-1} g^{-1} (about 7.8 × 10^{-4} M in the case of full extraction) and 2 mg l^{-1} (3.10 × 10^{-5} M) in soils and natural waters respectively.[13,39] Based on above-reported guideline values, we have tested the UV–vis response of ZnPC ligand (9.4 μM solution in THF) upon addition of Cu^{2+} ions from 0.01 equiv. to 4 equiv., which covers the lower among two permitted values reported above (in natural waters).

In Fig. 3A the UV–vis spectra of 9.4 μM ZnPC solution in THF in the presence of Cu^{2+} ions in the concentration range from 0.1 to 4 equivalents are shown. The ligand ZnPC showed an absorption peak
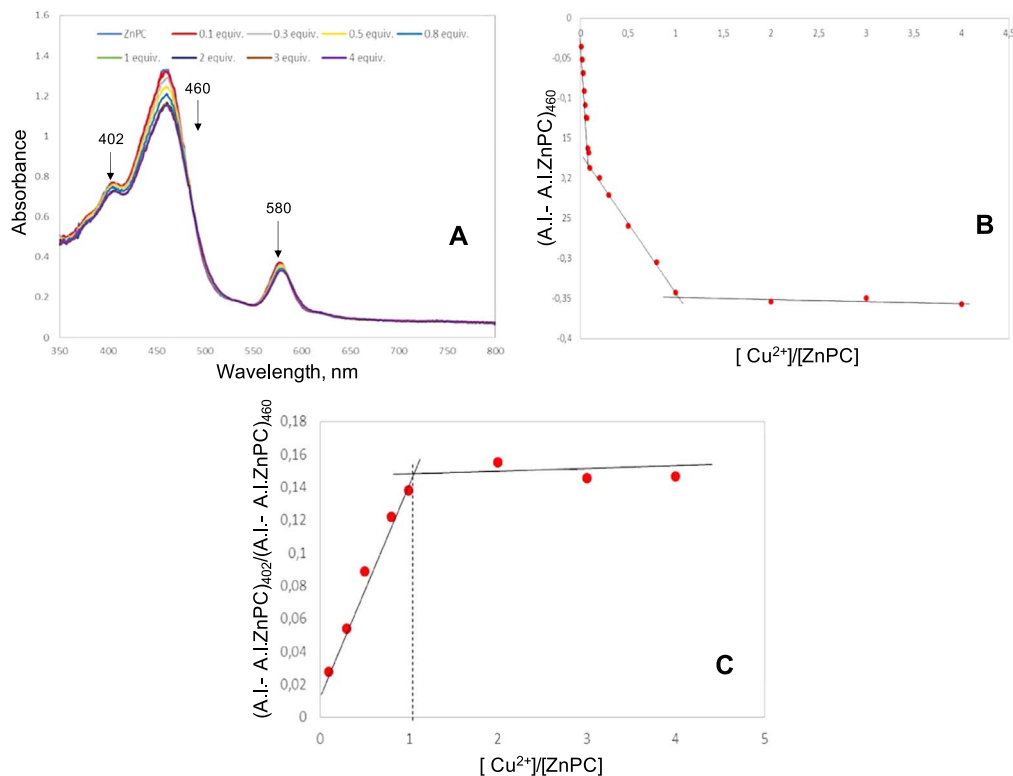
Figure 3. (A) UV–vis response of 9.4 μM ZnPC in THF in the presence of growing concentrations of Cu^{2+} -ions; (B) the absorbance at 460 nm and (C) the difference in absorbance intensity between 402 nm and 460 nm as function of $[Cu^{2+}]/[ZnPC]$. The arrows indicate the direction of absorbance upon addition of increasing amounts of cation.

at 460 nm and two smaller bands at 402 and 580 nm; the absorbance intensity of these peaks decreases gradually upon sequential addition of copper cations.

Figure 3B shows the variation of absorbance intensity of ZnPC at 460 nm in the presence of growing amount of Cu^{2+} ions. The linear correlation between copper ion concentration and variation of absorbance intensity during the complexation was found. On the calibration curve in coordinates Absorbance vs $[Cu^{2+}]/[ZnPC]$, equivalents ratio] at least two zones of linear responses in concentration range from 0.01 equiv. ($9.4\cdot10^{-8}$ M) to 0.1 equiv. ($9.4\cdot10^{-7}$ M) and from 0.1 equiv. to 1 equiv. ($9.4\cdot10^{-6}$ M) with correlation coefficients 0.988 and 0.998 respectively can be noticed. The obtained results indicate the possibility to determine the low concentration of copper cation at the levels of WHO guideline value in natural waters, corresponding to $3.10\cdot10^{-5}$ M.[13] Finally, in Fig. 3C the difference in absorbance intensity between 402 nm and 460 nm as function of $[Cu^{2+}]/[ZnPC]$ ratio is shown. The formation of a 1:1 complex between ZnPC and Cu^{2+} was observed during the titration of ligand solution with growing amounts of Cu^{2+}, thus demonstrating the utility of ZnPC for ratiome UV–vis detection of copper ions.

The results obtained by the UV–vis measurements for ZnPC in solution suggest the possibility of the ligand application inside polymeric sensing materials for optical assessment of metal ions. Hence, we have tested the optical response of TOP-plasticized membranes containing ZnPC and ZnTPP-BPI ligands in amount of 1 wt% together with different amounts of TpClPBK cation-exchanger, (0.5, 1 and 5 wt% respectively) in order to elucidate the ligand functioning mechanism and find out the sensing material with the best performance. The compositions of tested membranes are listed in Table I. Figure 4A shows a photogram of on-glass deposited membranes Mb1-Mb5 in individual solutions of Cu^{2+} ions in the concentration range from 6.6×10^{-7} and 2.4×10^{-2} mol l^{-1} at 0.01 M HEPES background, pH 7.4.

Considering the formation of a 1:1 metal-to-ligand adduct in THF as confirmed from UV–vis tests, at least the double molar excess of lipophilic anionic sites, $TpClPB^-$, with respect to the carrier concentration is required in order to guarantee the double-charged Cu^{2+} ions permeability inside the membrane and effective ion-exchange. It was found, that an addition of 5 wt% of TpClPBK in membrane Mb3 doped with ZnPC ligand resulted in highest membrane variation in individual solutions of Cu^{2+} ions in the concentration range from 6.6×10^{-7} to 2.4×10^{-2} mol l^{-1}. Moreover, the sensing membrane Mb3 color variation from reddish-green to intense red was visually observable by naked eye and was very well distinguished on web-cam taken post-processed images, Fig. 4A. The images variation was performed in terms of the picture sharpness (20% up in respect to original) and contrast (80%), the picture color temperature was not varied and corresponded to the standard digital camera color temperature of 6500 K. The digitalization of sensor optical response was performed through in-house written Matlab codes to interpret the membranes optical intensities in RBG color space. The optical intensity values were normalized to the glass background intensity without the sensing membrane, and the calibration curves were constructed by plotting the normalized optical intensity at red, green and blue color channels vs the logarithm of the Cu^{2+} ions concentration, Fig. 4B. The maximum change in intensity of membrane Mb3 was recorded for the green channel ($R_G^2 = 0.980$), which is complementary to the membrane Mb3 color. The lower and hardly quantifiable optical responses towards copper ions were registered for all other tested membranes (Fig. 4A), therefore the membrane Mb3 based on ZnPC and doped with a significant molar excess of TpClPBK cation-exchanger (1:15 ratio in respect to ligand) was selected for further studies as the best sensing material for Cu^{2+} assessment. The significant content of lipophilic anionic sites $TpClPB^-$ required to tune copper ions sensitivity of membrane Mb3 indicates a more complex ligand/target ion interaction mechanism in comparison to that observed in solution, and possible formation of intermediates of
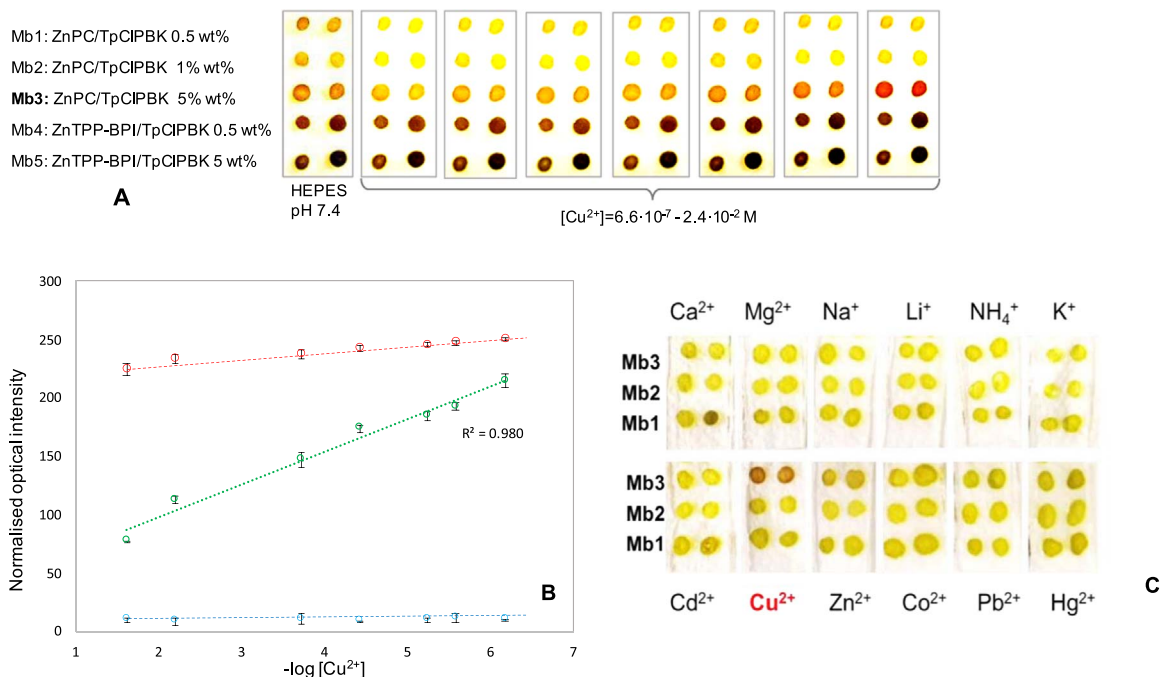
Figure 4. (A) Photogram showing the optical response of membrane Mb1-Mb5 based on ZnPC and ZnTPP-BPI ligands doped with different TpClPBK cation-exchanger amounts and deposited on glass transducer towards Cu^{2+} ion in the concentration range from 6.6×10^{-7} to 2.4×10^{-2} M at 0.01 M HEPES pH 7.4 background upon excitation with 380 nm LED. Images were taken by a webcam and post-processed in terms of the picture sharpness (20% up in respect to original) and contrast (80%), the picture color temperature is $T_{picture} = 6500$ K (B) Calibration curve of ZnPC-based membrane Mb3 in coordinates normalized by optical intensities of the red, green and blue channels vs - log $[Cu^{2+}]$; data extracted from a snapshot reported in Fig. 4A; (C) Colorimetric variation of optodes with membranes Mb1-Mb3 doped with ZnPC ligand after testing in different cations solutions of 2.4×10^{-2} mol l^{-1}.

varied stoichiometry. A detection limit of 4.7×10^{-7} M for Cu^{2+} (0.03 mg l^{-1}) ion^{-1} was estimated for membrane Mb3, a value about two orders of magnitude lower than WHO guideline value of 2 mg l^{-1} for natural waters. In order to assess the selectivity of the membranes Mb1- Mb3 doped with ZnPC ligand for Cu^{2+} ions, their response to copper ions was compared to that for other cations such as Na^+, K^+, Li^+, Ca^{2+}, Mg^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+} and NH_4^+. According to the Fig. 4C, the highest affinity to coordination of Cu^{2+} ions, accomplished with a visibly (naked eye) observed color change from green to intensive red was registered for membrane Mb3.

Encouraged by the ZnPC coordination behavior obtained in solution, and the selective optical (visual) response of polymeric membranes doped with these ligands, and deposited on glass transducers, we have investigated the possibility to go a step forward and investigate a possibility to apply developed polymeric membranes into paper-based optodes. Our choice of paper support was dictated by the aim to develop a low-cost optical sensor, permitting an express evaluation of copper ions in the environment, while present at hazardous levels. In fact, optical sensors permit a simple and rapid tracking of analyte even in complex, multicomponent matrices, since they have no need to be wired with the detector, often do not require sample pre-treatment and often may give useful response without power supply through "naked-eye" mode functioning. According to our previous studies on paper-based optical sensors,[35–37] we have decided to deposit the sensing spot of tested polymeric membranes directly onto filter paper strips. The paper strips were first treated with 0.01 M MES buffer solution at pH 5.5, in order to avoid a pH side-response of the optode and then 5 μl of the membrane cocktail in THF was deposited to form the sensing spot. ZnTPP-BPI-based membranes ZnTPP-BPI-based membranes Mb4 and Mb5 were deposited on the same paper strip in order to compare the performance of two ligands, while ZnPC-based membrane Mb1, containing the amount of TpClPBK cation-exchanger, unsufficient for cations promorion incide polymeric membrane phase, was excluded from on-paper tests.

In the present work we have selected the aqueous extracts of different topsoils in order to check the practical applicability of the developed on-paper optodes based on ZnPC and ZnTPP-BPI ligands for the selective Cu^{2+} detection. In soils copper is almost exclusively present in the divalent form in amount of about 5–50 mg kg^{-1}, most of which is present in occluded or lattice form. The concentration of free Cu^{2+} ions in the soil solution is lower and lies in the range of 1 $\times 10^{-5}$ to 6×10^{-4} M[40]; this concentration is immediately available for plant uptake, and directly related to the Cu^{2+} content in ground waters. Based on these values, considering the above-mentioned permissible levels for copper of 2 mg l^{-1} (3.1×10^{-5} M) in natural waters,[13] and the US EPA 50 μg l^{-1} (7.8×10^{-4} M) practical quantification limit for copper,[41] we have established in our experiments the borderline concentration of copper of 1 $\times 10^{-3}$ M; below this concentration the copper level in sample could be considered safe, while the higher Cu^{2+} ions concentration will indicate sample pollution. We have selected different sites for soil sampling, based on consideration that the pollution with copper in these sites can be significant, two different rubbish dumps (Ronciglione and Borgo val di Taro), the Ciampino airport runway, and two gas stations in Rome area. Moreover, we have tested soil samples from two private gardens and university garden. For five soil samples the amount of copper was previously evaluated by standard AAS method, and it was in the range from 0.338 to 46.9 m g kg^{-1}. Each sample was tested three times for two replicated spots of the same membrane (n = 3), and the estimated concentrations of copper ion were determined by the calibration curve. Photograms of the performed analysis are shown in Fig. 5, while results of the copper assessment are listed in Table II. The developed ZnPC- based optode with membrame Mb 3 was able to fastly asses the presence of copper ions in concentration higher than the established borderline concentration of 1×10^{-3} M in samples 3 (airport), 7 and 8 (fuel stations), but also a high copper concentration was detected in a soil sample 9, collected in the Tor Vergata University garden. The amounts of Cu^{2+} in aqueous extract of soil sample 3 were in agreement with the Cu^{2+} content estimated with standard AAS
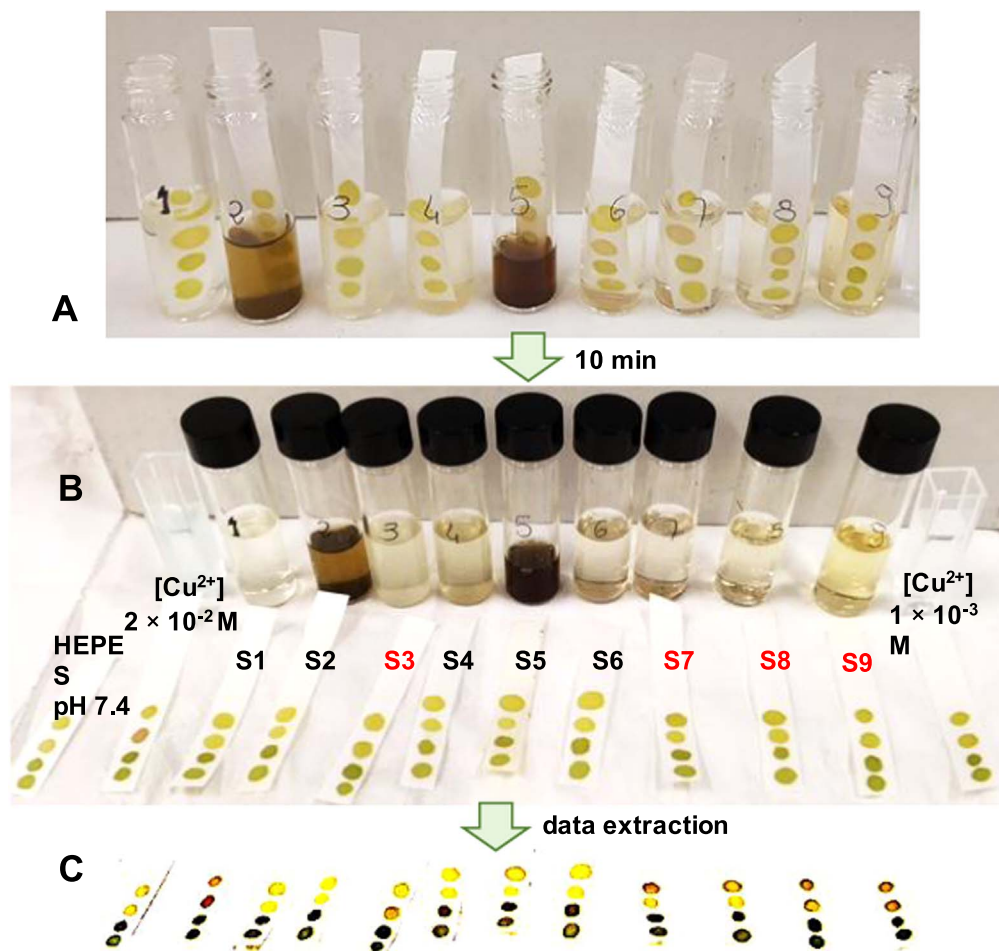
Figure 5. The smartphone taken photograms of Cu^{2+} colorimetric analysis in soils: (A) the image of the on-paper optodes immersed in samples extracts; (B) optodes response comparison after measurement; (C) the post-processed image used for data digitalisation. In Fig. 5C picture brightness and contrast are 8% and 80% up in respect to original, the picture color temperature is $T_{picture} = 6500$ K.

method, indicating the feasibility of ZnPC -based optodes for copper assessment in real samples.

Conclusions

Depending by its concentration, copper may be toxic for human being and environment. The development of accurate, cheap and easy to use system to monitor the presence of this heavy metal is fundamental to avoid environmental pollution or health damage. The results we obtained indicate that porphyrin-based ligands are suitable materials for detection of copper ion in soil or in water that can be performed by familiar device (smartphone camera) and with a disposable paper strips doped with a suitable chromophore. The main advantage of the developed optodes with respect official methods (as for example AAS) is that no particular processing step is required before the analysis, making possible to perform a real time monitoring process. Moreover, the system we developed allows detecting Cu^{2+} below the concentration limit suggested by WHO. Once more porphyrinoids showed their versatility as substrates to prepare organic film tailored for the sensing of different species; taking advantage by the outstanding optical properties of this class of macrocycle, we were able to prepare organic film tailored for the sensing of different species.

ORCID

Larisa Lvova ⓘ https://orcid.org/0000-0002-1137-6973
Federica Mandoj ⓘ https://orcid.org/0000-0001-6542-8110
Giuseppe Pomarico ⓘ https://orcid.org/0000-0003-3029-7063
Roberto Paolesse ⓘ https://orcid.org/0000-0002-2380-1404

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