- Supplementary Information -

Smart sensory material for divalent cations: dithizone immobilized membrane for optical analysis

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Table of contents

S1. Kinetics profiles of Cu(II), Hg(II) and Zn(II) on mem-DTZ

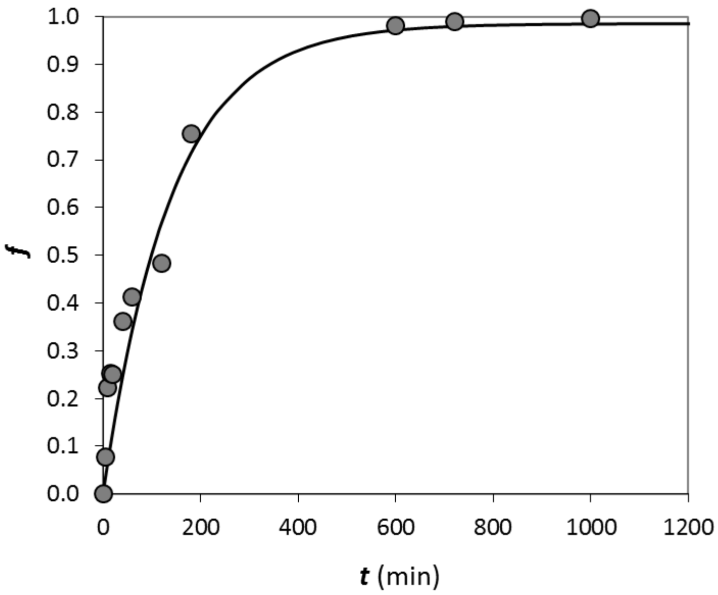

Figure s1. Sorption kinetic of Cu(II) on mem-DTZ. V = 10 mL; w = 0.025 g mem-DTZ (1×2 cm); Cu(II) 8.1 μM, pH = 2, I =0.1 M HCl/KCl

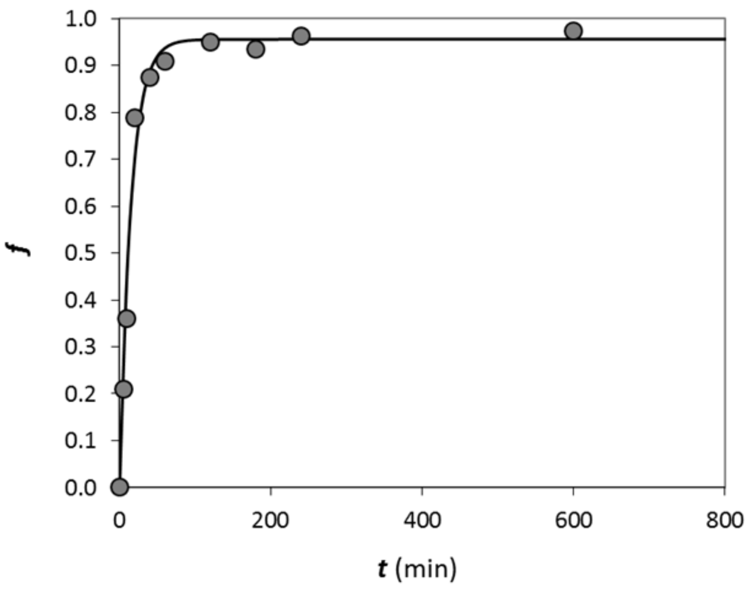

Figure s2 Sorption kinetic of Hg(II) on mem-DTZ. V = 10 mL; w = 0.025 g mem-DTZ (1×2 cm); Hg(II) 0.7 μM, pH = 2, I =0.1 M HCl/KCl

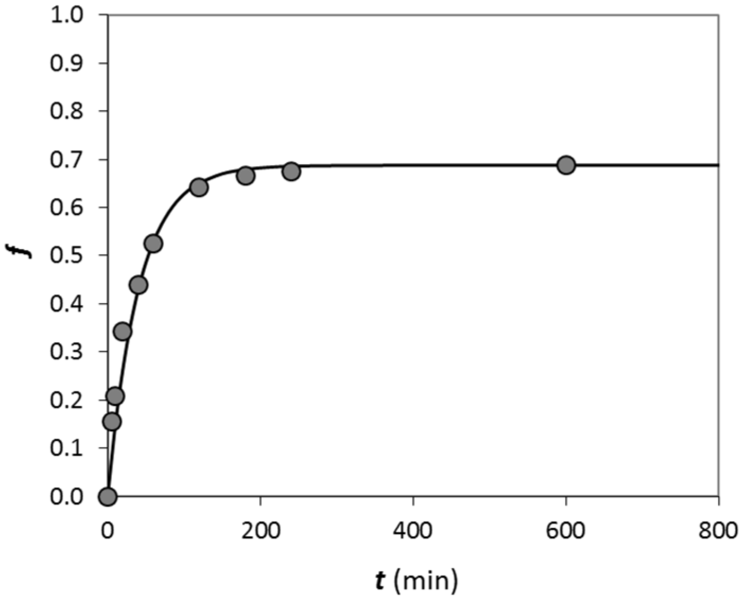

Figure s3 Sorption kinetic of Zn(II) on mem-DTZ. *V* = 10 mL; *w* = 0.025 g mem-DTZ (1×2 cm); Zn(II) 6.1 μM, pH = 4.5, I =0.1 M KCl

S2. Sorption isotherms of Cd(II), Hg(II) and Zn(II) on mem-DTZ

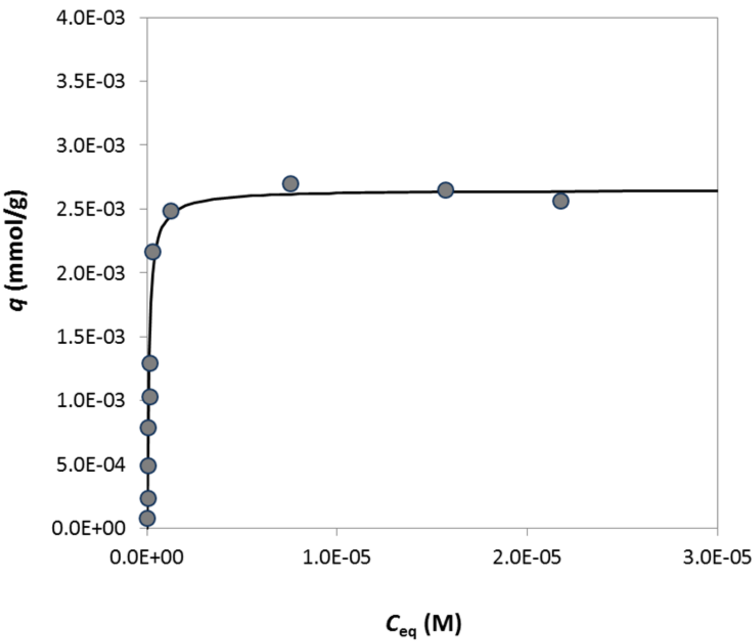

Figure s4 Sorption isotherm of Cd(II) on mem-DTZ. *V* = 10 mL; *w* = 0.025 g mem-DTZ (1×2 cm); Cd(II) solutions from 0 to 45 μM, pH = 4.5, I =0.1 M KCl. The continuous line is the best fitting obtained applying eq.2, by nonlinear regression. Fitting parameters: K_L =1.0(3)×10^7 mol L^{-1} and q_{max} = 2.7(2)×10^{-3} mmol g^{-1}

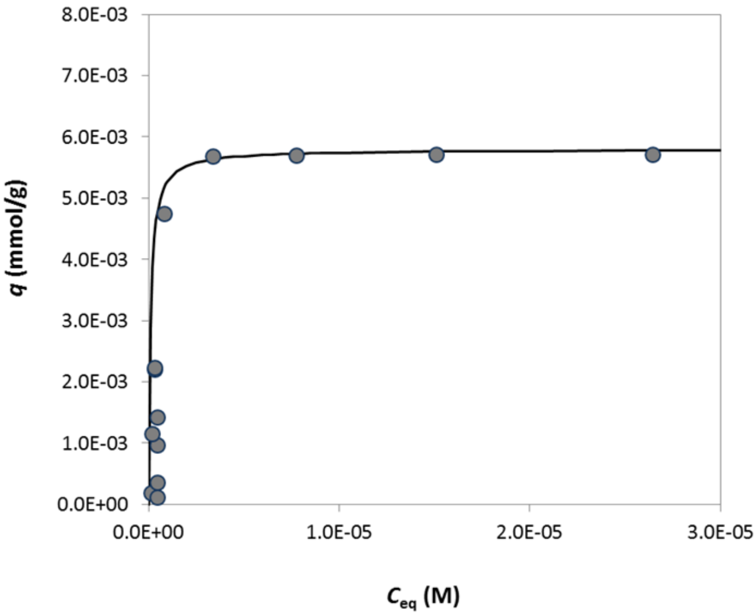

Figure s5 Sorption isotherm of Hg(II) on mem-DTZ. V = 10 mL; w = 0.025 g mem-DTZ (1×2 cm); Hg(II) solutions from 0 to 30 μM, pH = 2, I =0.1 M HCl/KCl. The continuous line is the best fitting obtained applying eq.2, by nonlinear regression. Fitting parameters: K_L =1.0(6)×10^7 mol L^{-1} and q_{max} = 5.8(2)×10^{-3} mmol g^{-1}

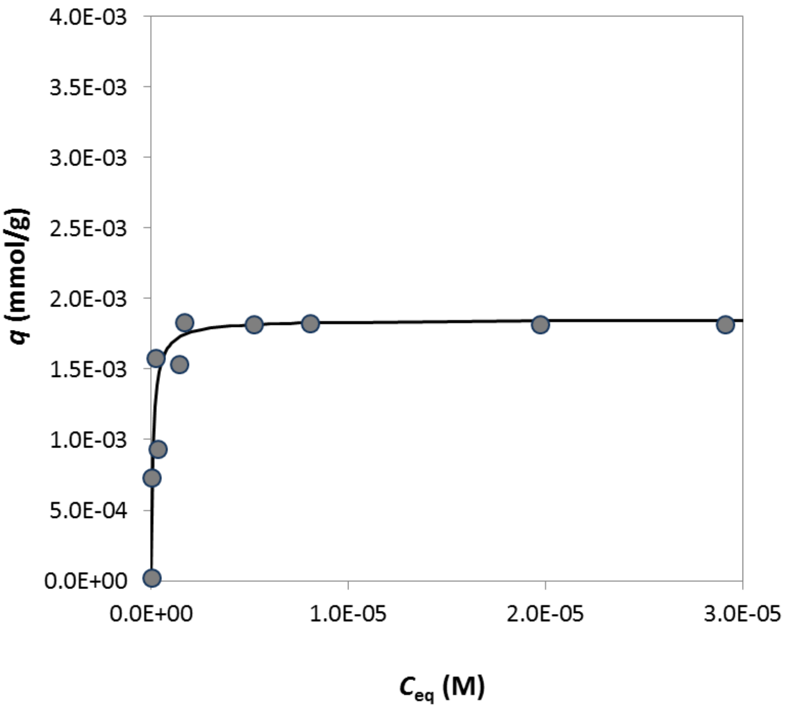

Figure s6 Sorption isotherm of Zn(II) on mem-DTZ. V = 10 mL; w = 0.025 g mem-DTZ (1×2 cm); Cd(II) solutions from 0 to 45 μM, pH = 4.5, I =0.1 M KCl. The continuous line is the best fitting obtained applying eq.2, by nonlinear regression. Fitting parameters: K_L =1.0(5)×10^7 mol L^{-1} and q_{max} = 1.9(2)×10^{-3} mmol g^{-1}. Since at pH 4.5 the maximum percentage of Zn(II) that can be sorbed on the mem-DTZ is around 70% (see sorption profiles, Figure s...) a value of q_{max} lower of that found for the other cations was expected

S3. Sorption profiles of Cd(II), Cu(II), Hg(II) and Zn(II) on mem-DTZ

S3.1 – System Cd(II)/mem-DTZ

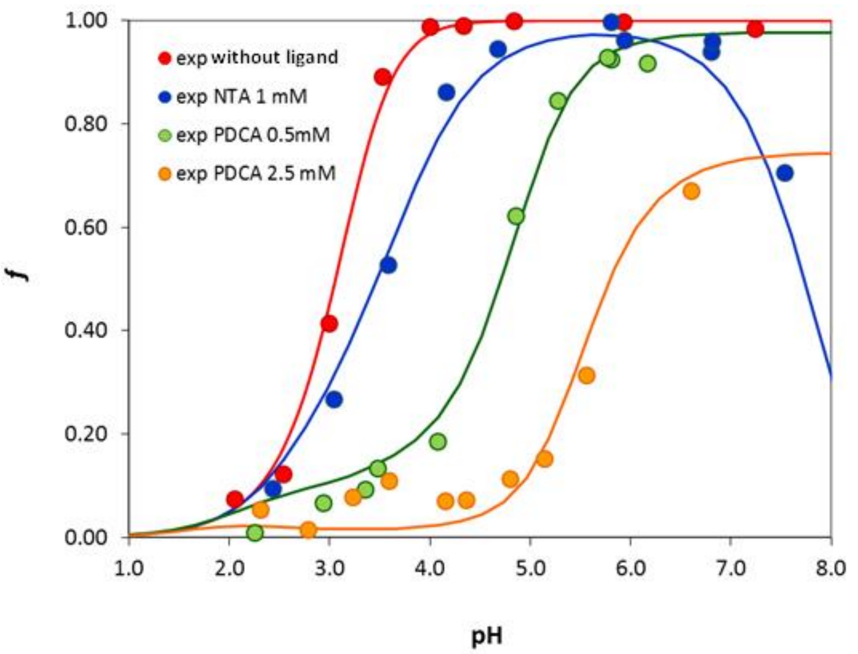

Figure s7 Sorption profiles of Cd(II) on mem-DTZ. *V* = 10 mL; *w* = 0.025 g mem-DTZ; ● profile without ligand in solution, Cd(II) 1.9 μM, I =0.1 M KCl. ● profile with NTA1 mM, Cd(II) 1.9 μM, I =0.1 M KCl. ● profile with PDCA 0.5 mM, Cd(II) 1.8 μM, I =0.1 M KCl. ● profile with PDCA 2.5 mM, Cd(II) 1.8 μM, I =0.1 M KCl

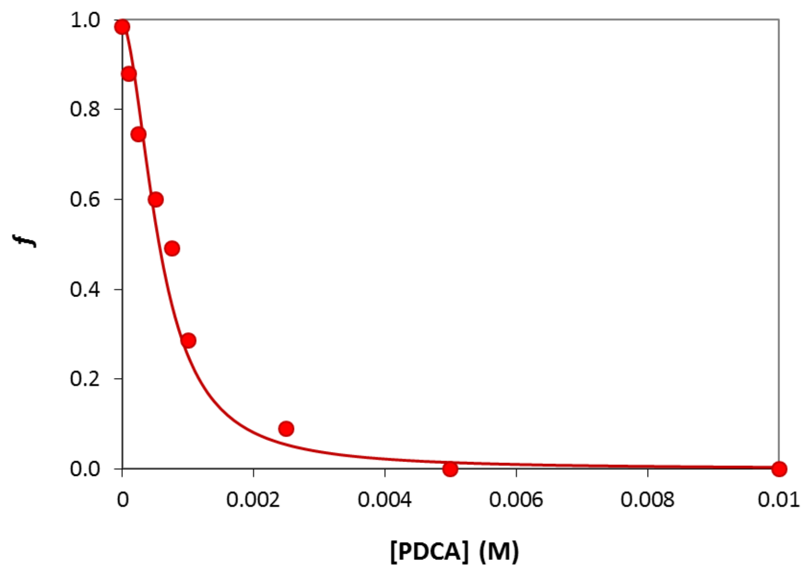

Figure s8 Desorption profile of Cd(II) on mem-DTZ using as extractant PDCA. *V* = 10 mL; *w* = 0.025 g mem-DTZ. PDCA from 0 a 0.01 M; Cd(II) 1.9 μM; pH = 4.5; I =0.1 M KCl

Continuous lines in Figures s7 and s8 were obtained by considering the following complexation reactions in solid phase and the corresponding exchange coefficients

$$\mathrm{Cd} + \overline{\mathrm{DTZ}} \rightleftarrows \overline{\mathrm{CdDTZ}}$$

$$\mathrm{Cd} + 2\,\overline{\mathrm{DTZ}} \rightleftarrows \overline{\mathrm{Cd(DTZ)_2}}$$

	log β_{110ex}	log β_{110i}	log β_{120ex}	log β_{120i}
Cd(II)	7.57(1)	8.00(1)	12.9(2)	13.1(2)

(The values of the exchange coefficients (at I=0.1 M) and intrinsic complexation constants reported are the media of the data obtained in the different experiments of Figures s7 and s8. Numbers in parenthesis are the standard deviation on the last digits).

S3.2 – System Cu(II)/mem-DTZ

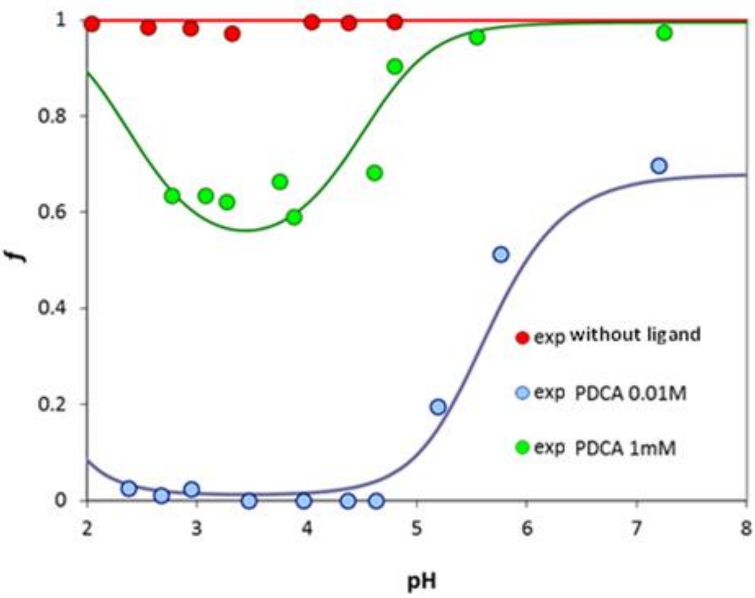

Figure s9 Sorption profiles of Cu(II) on mem-DTZ. *V* = 10 mL; *w* = 0.025 g mem-DTZ; ● profile without ligand in solution, Cu(II) 3.8 μM, I =0.1 M KCl. ● with PDCA 0.01M, Cu(II) 3.7 μM, I = 0.1 M KCl ● profile with PDCA 1.0 mM, Cu(II) 4.2 μM, I =0.1 M KCl

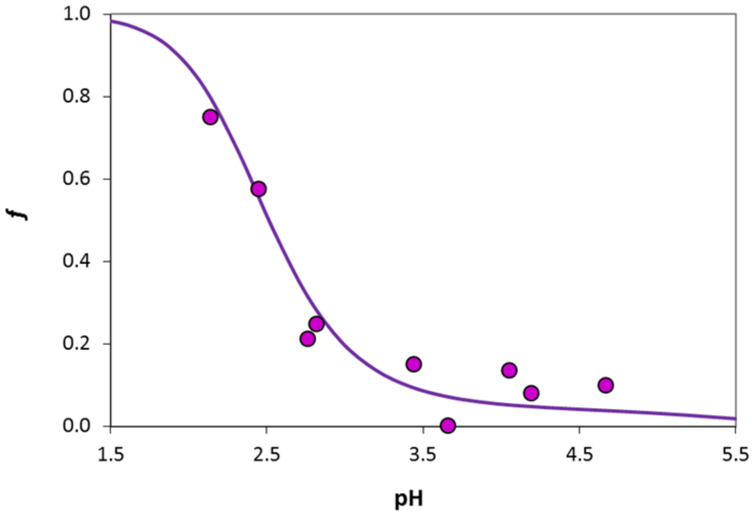

Figure s10 Sorption profiles of Cu(II) on mem-DTZ in presence of CDTA in solution. *V* = 10 mL; *w* = 0.025 g mem-DTZ, CDTA 1 mM, Cu(II) 4.0 µM, I =0.1 M KCl

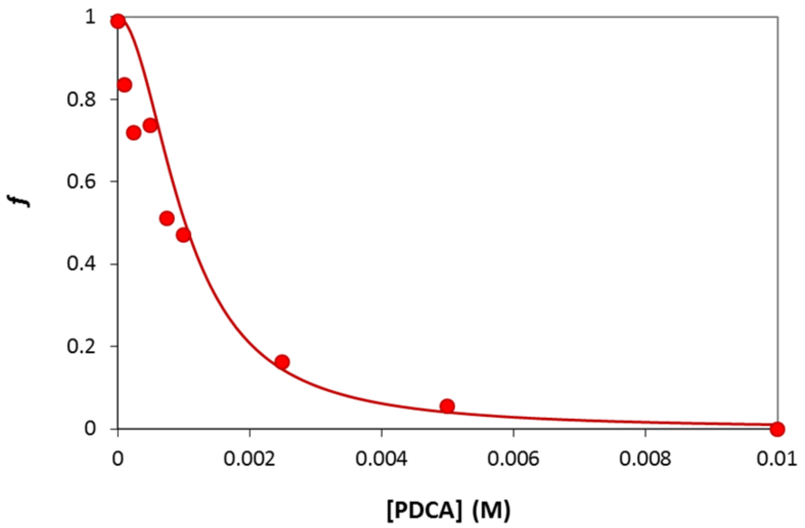

Figure s11 Desorption profile of Cu(II) on mem-DTZ using as extractant PDCA. *V* = 10 mL; *w* = 0.025 g mem-DTZ. PDCA from 0 a 0.01 M; Cu(II) 7.7 µM; pH = 2; I =0.1 M HCl/KCl

Continuous lines in Figures s10 and s11 were obtained by considering the following complexation reactions in solid phase and the corresponding exchange coefficients

$$\mathrm{Cu} + \overline{\mathrm{DTZ}} \rightleftarrows \overline{\mathrm{CuDTZ}}$$

$$\mathrm{Cu} + 2\,\overline{\mathrm{DTZ}} \rightleftarrows \overline{\mathrm{Cu(DTZ)_2}}$$

	log β_{110ex}	log β_{110i}	log β_{120ex}	log β_{120i}
Cu(II)	9.35(1)	9.79(1)	19.64(5)	19.86(5)

(The values of the exchange coefficients (at I=0.1 M) and intrinsic complexation constants reported are the media of the data obtained in the different experiments of Figures s10 and s11. Numbers in parenthesis are the standard deviation on the last digits).

S3.3 – System Hg(II)/mem-DTZ

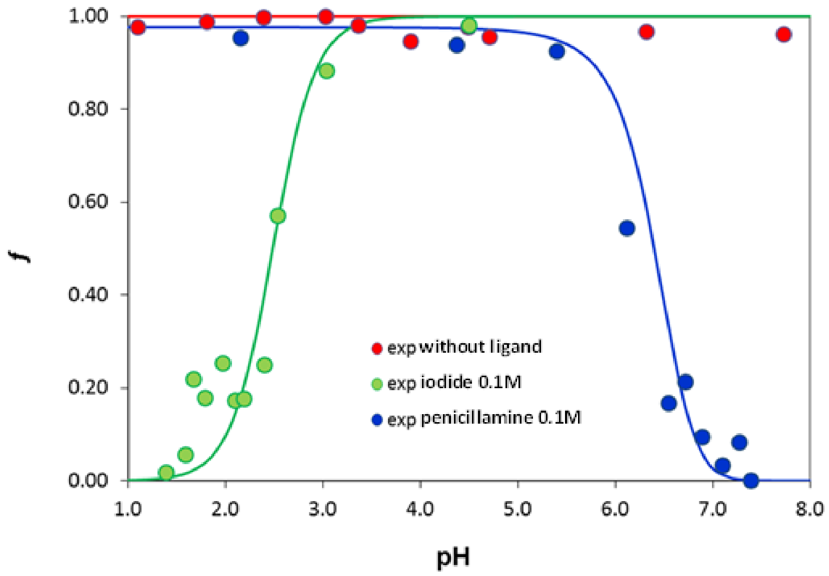

Figure s12 Sorption profiles of Hg(II) on mem-DTZ. V = 10 mL; w = 0.025 g mem-DTZ; ● profile without ligand in solution, Hg(II) 5.7 µM, I =0.1 M KCl. ● with penicillamine 0.1M, Hg(II) 9.5 µM, I = 0.1 M KCl ● profile with iodide 1.0 mM, Hg(II) 9.5 µM, I =0.1 M KCl

Continuous lines in Figures s12 were obtained by considering the following complexation reactions in solid phase and the corresponding exchange coefficients

$$\mathrm{Hg} + \overline{\mathrm{DTZ}} \rightleftarrows \overline{\mathrm{HgDTZ}}$$

$$\mathrm{Hg} + 2\,\overline{\mathrm{DTZ}} \rightleftarrows \overline{\mathrm{Hg(DTZ)_2}}$$

	log β_{110ex}	log β_{110i}	log β_{120ex}	log β_{120i}
Hg(II)	20.64(2)	21.09(2)	39.4(8)	39.6(8)

(The values of the exchange coefficients (at I=0.1 M) and intrinsic complexation constants reported are the media of the data obtained in the different experiments of Figures s10 and s11. Numbers in parenthesis are the standard deviation on the last digits).

S3.4 – System Zn(II)/mem-DTZ

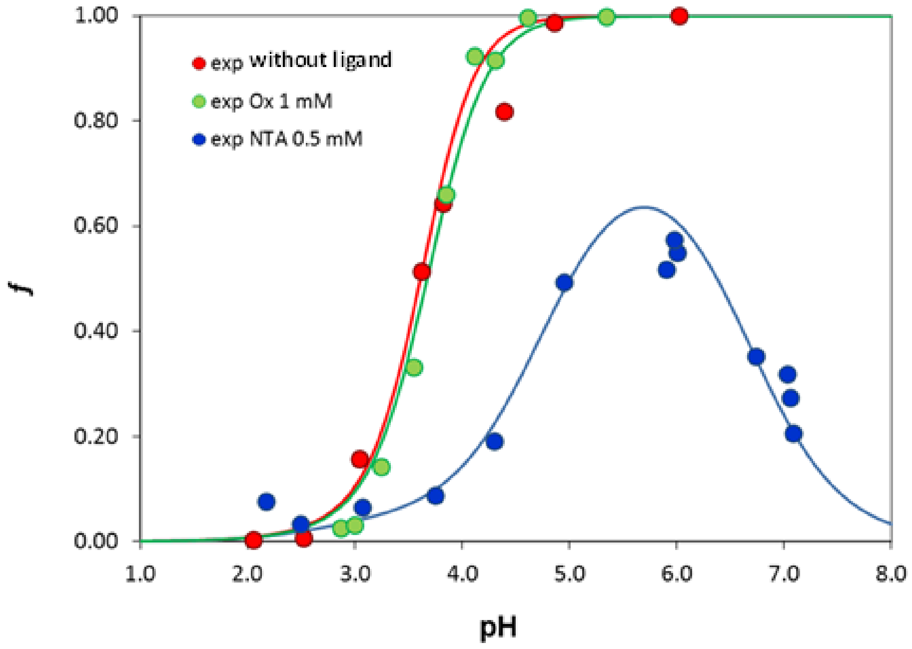

Figure s13 Sorption profiles of Zn(II) on mem-DTZ. *V* = 10 mL; *w* = 0.025 g mem-DTZ; ● profile without ligand in solution, Zn(II) 3.9 µM, I =0.1 M KCl. ● with NTA 0.5 mM, Zn(II) 3.3 µM, I = 0.1 M KCl ● profile with oxalate 1.0 mM, Zn(II) 3.2 µM, I =0.1 M KCl

Continuous lines in Figures s13 were obtained by considering the following complexation reactions in solid phase and the corresponding exchange coefficients

$$\mathrm{Zn} + \overline{\mathrm{DTZ}} \rightleftarrows \overline{\mathrm{ZnDTZ}}$$

$$\mathrm{Zn} + 2\,\overline{\mathrm{DTZ}} \rightleftarrows \overline{\mathrm{Zn(DTZ)_2}}$$

	log β_{110ex}	log β_{110i}	log β_{120ex}	log β_{120i}
Zn(II)	6.93(2)	7.37(2)	12.0(1)	12.2(1)

(The values of the exchange coefficients (at I=0.1 M) and intrinsic complexation constants reported are the media of the data obtained in the different experiments of Figures s10 and s11. Numbers in parenthesis are the standard deviation on the last digits).

S4. Colorimetric dose-response curve for Cu(II), Cd(II) and Hg(II) on mem-DTZ

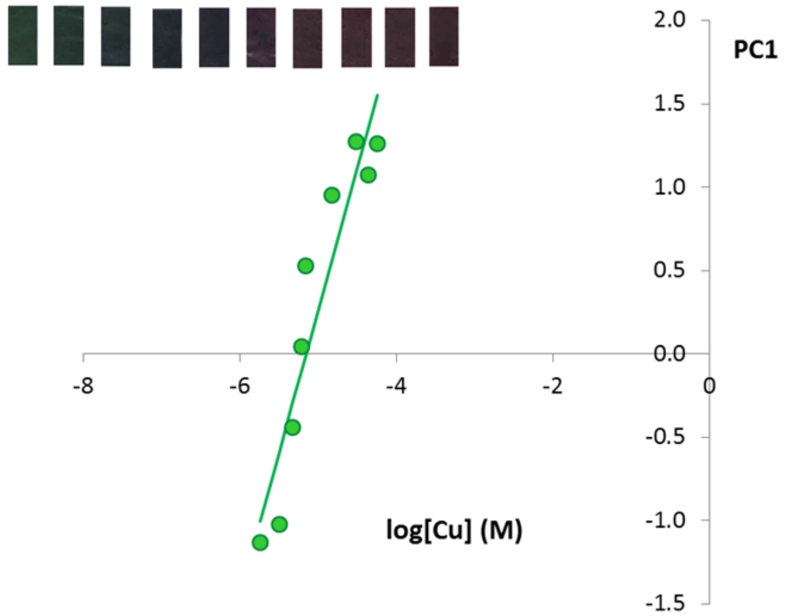

Figure s14 Colorimetric dose-response curve for Cu(II) on mem-DTZ. Top of the graph: digital pictures of the sensory membranes, taken after dipping in aqueous solutions of Cu(II) at increasing concentration.
V = 10 mL, *w* = 0.025 g mem-DTZ (1×2 cm), pH =2, I = 0.1 M HCl/KCl

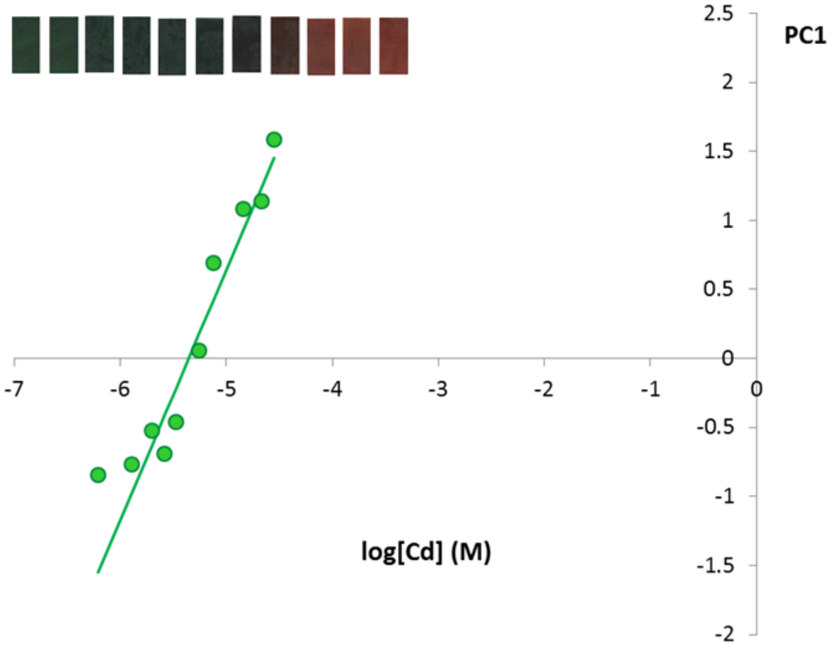

Figure s15 Colorimetric dose-response curve for Cd(II) on mem-DTZ. Top of the graph: digital pictures of the sensory membranes, taken after dipping in aqueous solutions of Cd(II) at increasing concentration.
V = 10 mL, *w* = 0.025 g mem-DTZ (1×2 cm), pH = 5, I = 0.1 M KCl.

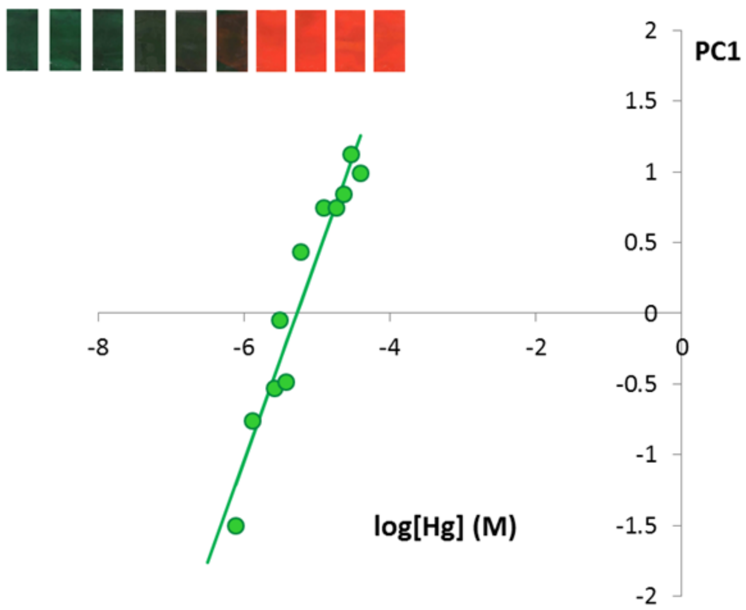

Figure s16 Colorimetric dose-response curve for Hg(II) on mem-DTZ. Top of the graph: digital pictures of the sensory membranes, taken after dipping in aqueous solutions of Hg(II) at increasing concentration.
V = 10 mL, *w* = 0.025 g mem-DTZ (1×2 cm), pH =2, I = 0.1 M HCl/KCl.

S5. Colorimetric standard addition method for Cu(II), Cd(II) and Hg(II) in real samples

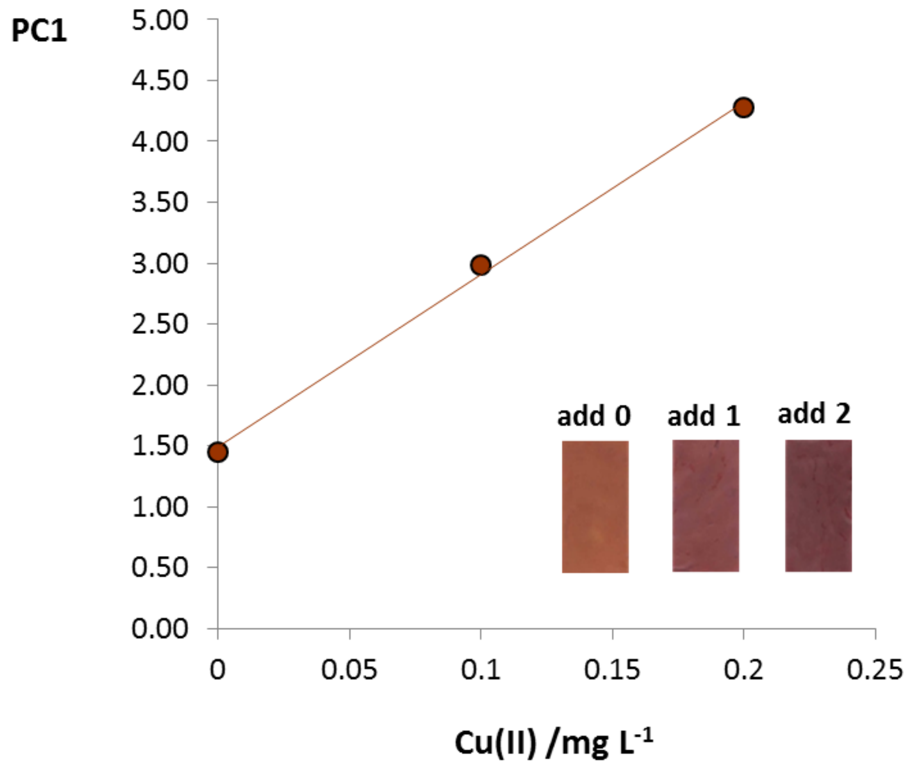

Figure s17 Determination of Cu(II) in the reference material “Sewage Sludge CC136A”: standard additions method applied to the solution obtained by mineral digestion of the solid sample (see paragraph 2.2.5). V = 15 mL of the three times diluted sample solution; w = 0.025 g mem-DTZ (1×2 cm); pH = 2. Linear regression fit: $y = 14.1(7) \cdot x + 1.49(8)$ ($R^2 = 0.997$)

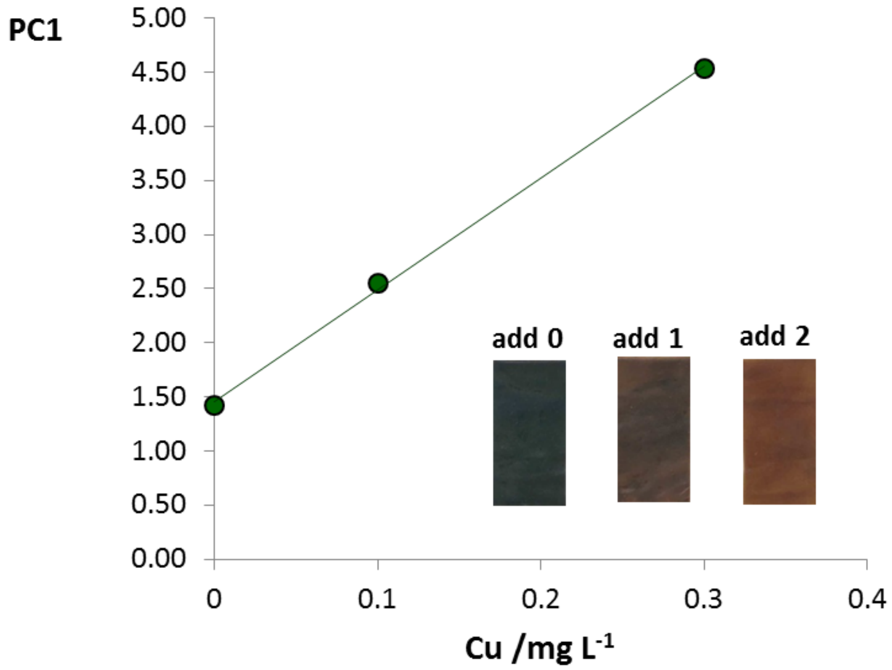

Figure s18 Determination of Cu(II) in a commercial white wine (Ronco San Crispino, Italy): standard additions method. V = 20 mL; w = 0.025 g mem-DTZ (1×2 cm); pH = 3.6. Linear regression fit: $y = 10.3(3) \cdot x + 1.46(6)$ ($R^2 = 0.999$)

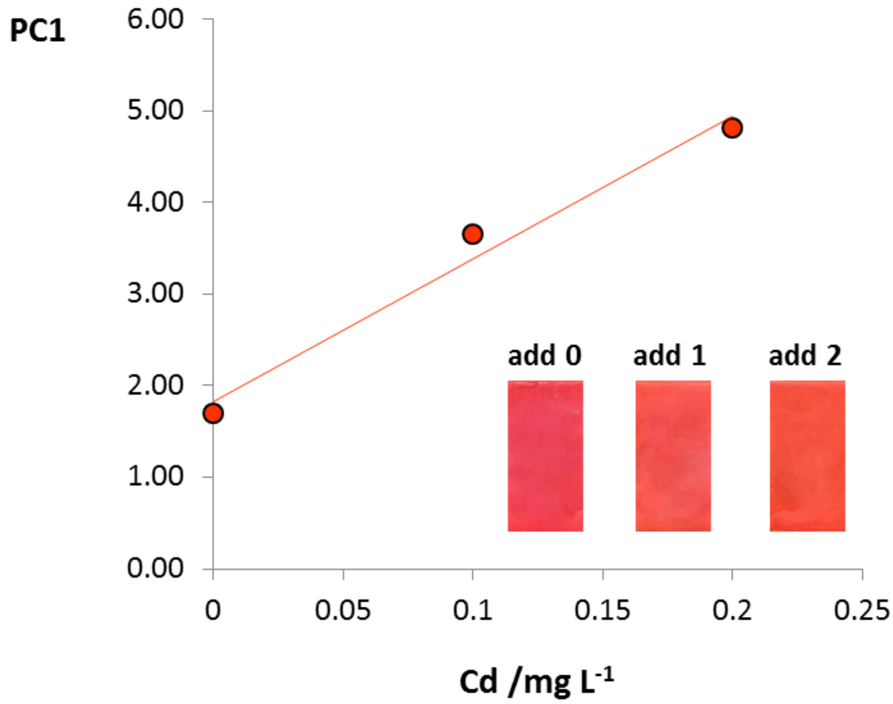

Figure s19 Determination of Cd(II) in spiked tap water (spike 0.1 mg L^{-1} Cd(II)): standard additions method. V = 50 mL; w = 0.025 g mem-DTZ (1×2 cm); pH = 8.1. Linear regression fit: $y = 15(2) \cdot x + 1.8(3)$ ($R^2 = 0.980$)