Electronic Supplementary Information

Sub-ppm quantification of Hg(II) in aqueous media using both the naked eye and digital information from pictures of a colorimetric sensory polymer membrane taken with the digital camera of a conventional mobile phone

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S1. Materials

The following materials and solvents were commercially available and used as received unless otherwise indicated: Rhodamine B (Aldrich, 97%), triethylamine (Fluka, 98%), 1,3-propanediamine (Aldrich, 99%), methacryloyl chloride (Alfa Aesar, 97%), ethanol (VWR, 99.9%), dimethoxy-2-phenyl acetophenone (Aldrich, 99%), 2-hydroxyethyl acrylate (**1**) (Aldrich, 96%), ethylene glycol dimethacrylate (**3**) (Aldrich, 98%), and deuterated chloroform (VWR, 99.1%).

S2. Monomer Synthesis

The monomer *N-(3-(3',6'-bis(diethylamino)-3-oxospiro[isoindoline-1,9'-xanthen]-2-yl)propyl)methacrylamide* (**2**) was synthesized and purified following a previously described procedure.[1] The overall synthesis of the monomer and its characterization is shown in Scheme S1.
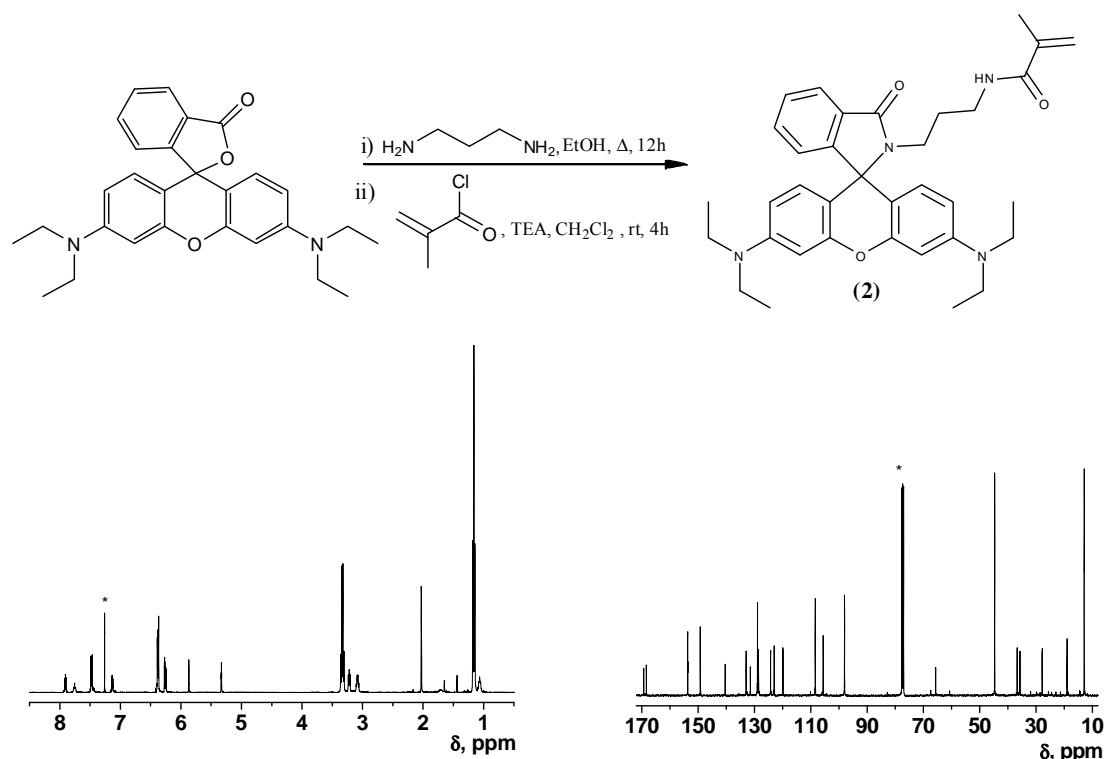
Scheme S1. Top: synthesis and chemical structure of the sensory monomer (**2**). Bottom: ^{1}H NMR (left) and ^{13}C NMR (right) of **2** (* = solvent signals, CDCl$_3$)

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[1] H. El Kaoutit, P. Estévez, S. Ibeas, F. C. García, F. Serna, F. B. Benabdelouahab and J. M. García, *Dyes Pigments*, 2013, **96**, 414.

S3.   Membrane Preparation

The membranes were prepared by radical polymerization of mixtures of the 2 different co-monomers (**1** and **2**) using ethylene glycol dimethacrylate (**3**) as cross-linking agent (1%) and dimethoxy-2-phenyl acetophenone (1.56 wt.%) as radical photoinitiator and a mercury-vapour lamp as a ultraviolet radiation source (365nm). Three different polymer films were prepared in this fashion by varying the molar concentration of the sensory monomer **2** (1, 2.5, and 5 % -see manuscript, Fig. 1-). The reactions were performed in silanised glass moulds of 100 µm thickness in an oxygen-free atmosphere at 65ºC for 5 h. Upon demoulding, the film was air dried for two days and overnight under vacuum at rt.

S4.   Measurements

UV/Vis spectra were recorded using a Varian Cary3-Bio UV/Vis spectrophotometer. Fluorescence spectra were recorded using a Hitachi F-7000 Fluorescence Spectrophotometer. Millipore-Q water was used to prepare the solutions. The concentration of Hg(II) in tap water (0.35 ppb $\pm$ 0.01) was determined by means of inductively coupled plasma mass spectrometry (ICP, Agilent 7500 i) by the Analytical Service of the Scientific Park at the University of Burgos. Sensing measurements performed in water were performed at acid, neutral, and basic pH (pH = 2, KCl-HCl; pH = 7 and pH = 9, TRIS-HCl). Apparent response time was recorded taking UV/Vis or fluorescence spectra at given times. The water-swelling percentage (WSP), the weight percentage of water uptake by the films upon soaking until equilibrium, in pure water, was obtained from the weights of a dry (w_d) and a water-swelled (the membranes was immersed in pure water at 20ºC until the swelled equilibrium was achieved) sample film (w_s) as follows: $100x[(w_s-w_d)/w_d]$.

S5. Spirolactam ring-opening process for Rho B derivative

non-fluorescent, colorless
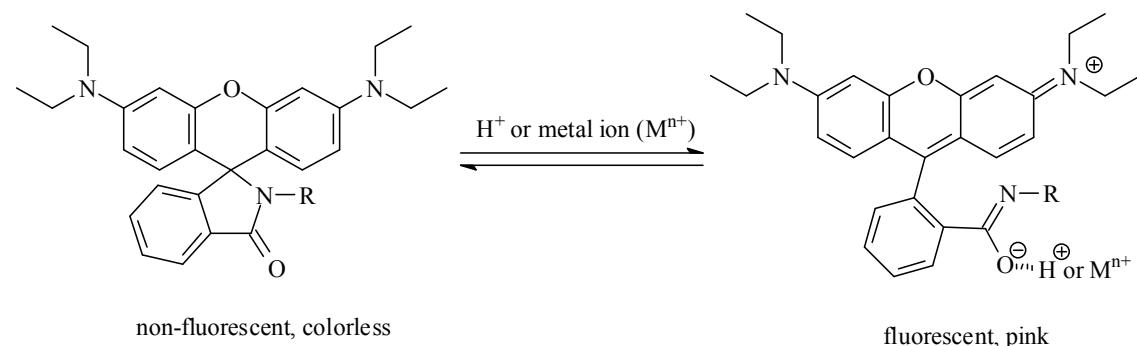
fluorescent, pink

Scheme S2. Spirolactam ring-opening process for a Rho B derivative, summarized by Beija *et al.* in a review of Rhodamine derivatives as fluorescent probes.[2]

S6. Digital pictures of strips of membranes Mem1% and Mem5% after dipping them into water containing different concentration of Hg(II) upon irradiation with a lab UV lamp.
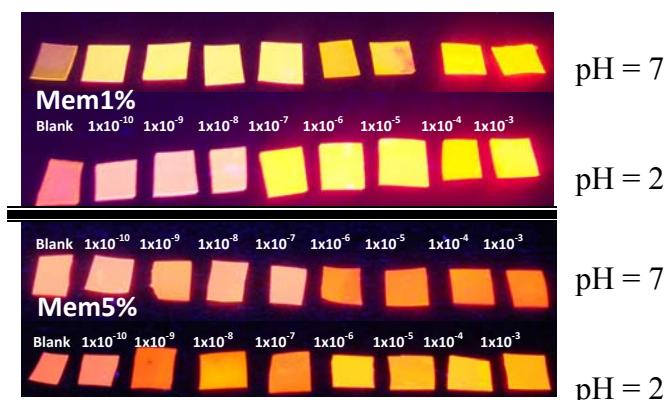
Fig. S1. Digital pictures of strips of membranes **Mem1%** and **Mem5%** after dipping them for 25 min into water containing different concentration of Hg(II) upon irradiation with a lab UV lamp (irradiation wavelength = 365nm). The molar concentration of Hg(II) is written on each membrane strip.

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[2] M. Beija, C. A. M. Afonso and J. M. G. Martinho, *Chem. Soc. Rev.*, 2009, **38**, 2410.

S7.　　Titration of Hg(II) in water media with membrane Mem1%
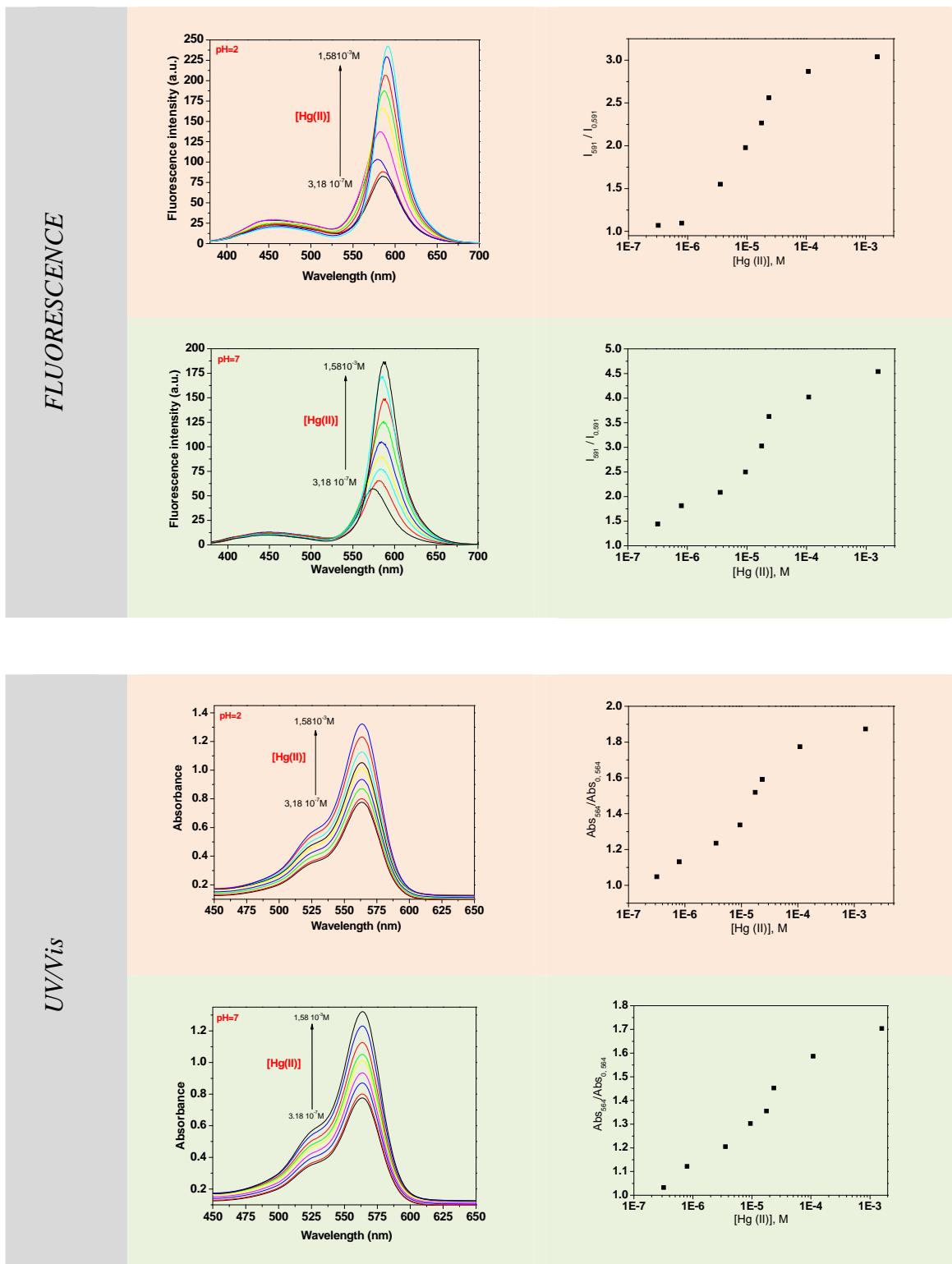
Fig. S2. UV/Vis and fluorescence titration curves of Hg(II) in water media with membrane **Mem1%**.

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S8.   Titration of Hg(II) in water media with membrane Mem2.5%
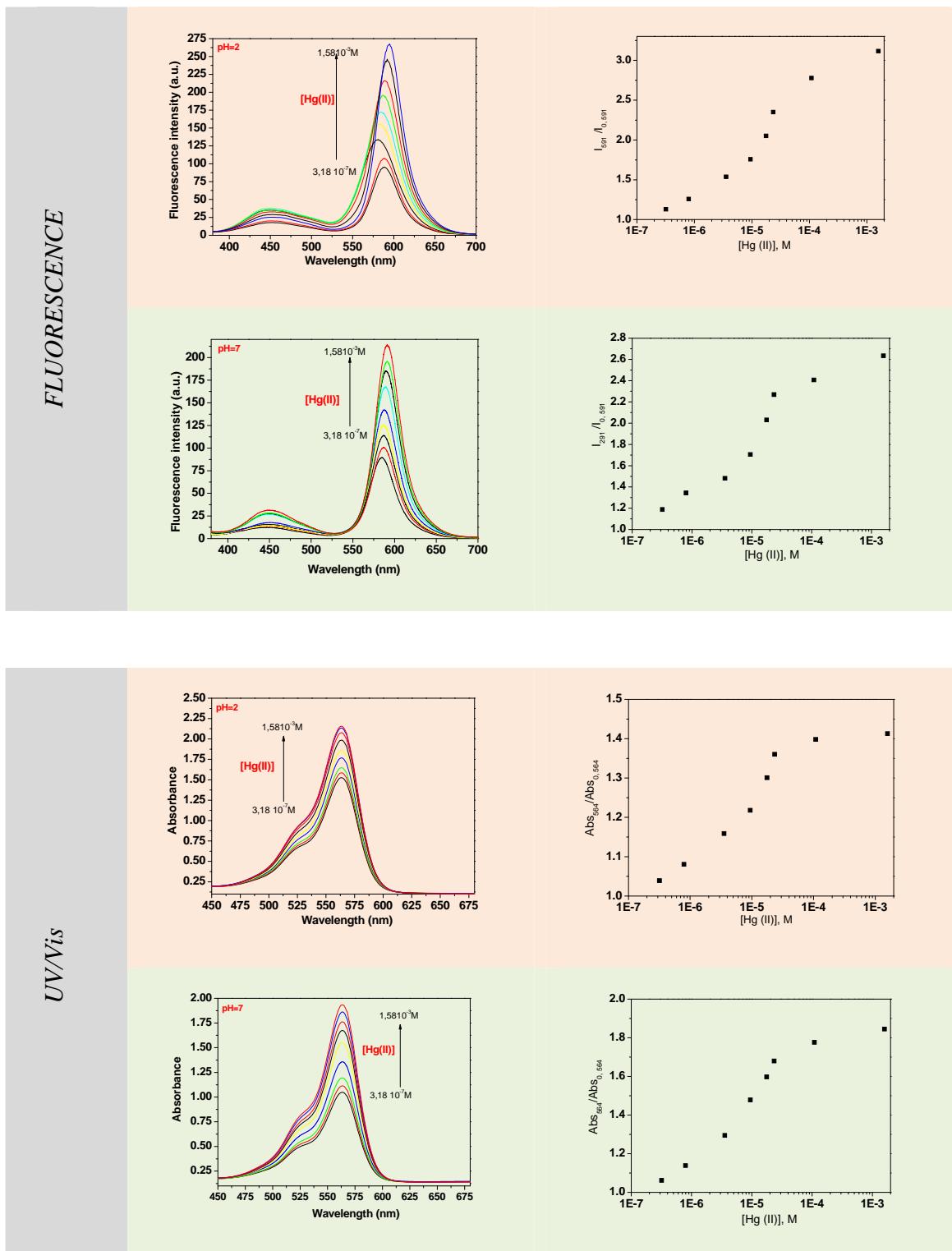
Fig. S3. UV/Vis and fluorescence titration curves of Hg(II) in water media with membrane **Mem2.5%**.

S9.   Titration of Hg(II) in water media with membrane Mem5%
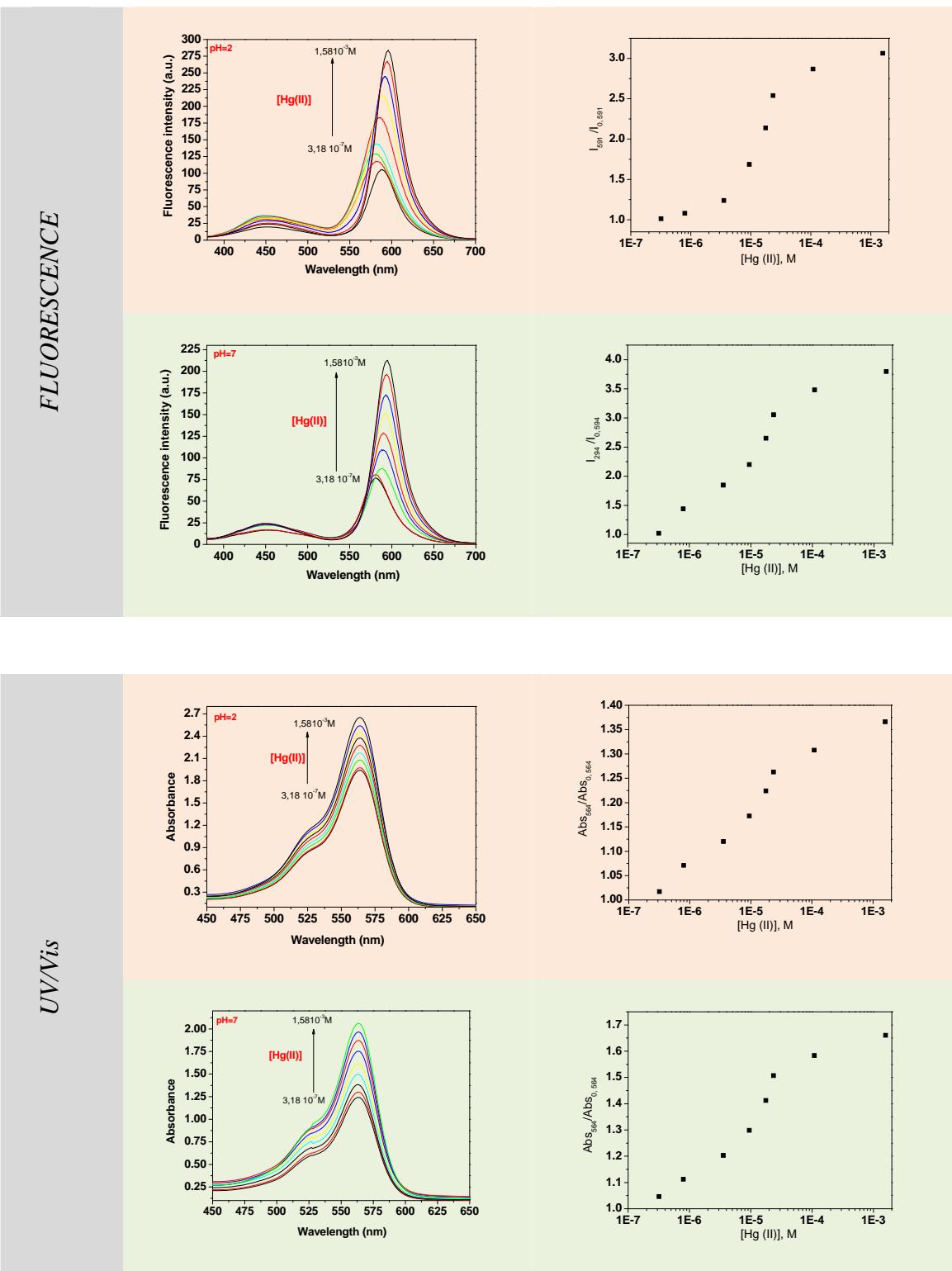
Fig. S4. UV/Vis and fluorescence titration curves of Hg(II) in water media with membrane **Mem5%**.

S10. Principal component analysis (PCA) of the RGB data of pictures of membranes dipped in water containing different quantities of Hg(II).

Mem1%. pH = 2.

| [Hg(II)], mol/L	Camera: mobile Samsumg Galaxy				Camera: digital camera SONY DSC-W100			
	RGB parameters				RGB parameters			
	R	G	B	PC1#	G	G	B	PC1#
0	154	110	109	-1.926	142	90	120	-1.613
1×10^{-10}	165	106	122	-1.832	152	89	134	-1.607
1×10^{-9}	170	108	121	-1.560	156	94	136	-1.606
1×10^{-8}	180	91	119	-0.684	166	78	136	-0.824
1×10^{-7}	183	36	93	1.428	177	31	128	1.003
1×10^{-6}	183	38	95	1.281	180	33	131	1.016
1×10^{-5}	177	43	100	0.713	174	34	132	0.672
1×10^{-4}	186	44	75	2.072	178	28	103	2.001
1×10^{-3}	165	38	93	0.508	160	27	111	0.959

PCA#

Component	Eigenvalue	% total variance	Cumul. %
PC1	2.3388	77.960	77.960
PC2	0.524306	17.477	95.437
PC3	0.136894	4.563	100.000

PCA weights#

	PC1
R	0.51887
G	-0.619211
B	-0.589365

PCA#

Component	Eigenvalue	% total variance	Cumul. %
PC1	1.98172	66.057	66.057
PC2	0.916703	30.557	96.614
PC3	0.101581	3.386	100.000

PCA weights#

	PC1
R	0.595653
G	-0.690703
B	-0.410032

The values of the variables in the equation are standardized subtracting the mean and dividing by their standard deviations.

Mem1%. pH = 7.

[Hg(II)], mol/L	Camera: mobile Samsumg Galaxy				Camera: digital camera SONY DSC-W100			
	RGB parameters				RGB parameters			
	R	G	B	PC1#	G	G	B	PC1#
0	155	118	111	-2.288	141	96	121	-2.411
1×10^{-10}	167	108	116	-1.524	154	88	129	-1.431
1×10^{-9}	173	84	117	-0.522	161	69	134	-0.381
1×10^{-8}	174	74	100	0.496	163	59	125	0.116
1×10^{-7}	186	75	112	0.716	177	62	137	0.847
1×10^{-6}	179	86	76	1.568	172	68	100	0.680
1×10^{-5}	172	93	108	-0.415	169	76	127	-0.028
1×10^{-4}	171	46	101	1.023	169	34	129	1.300
1×10^{-3}	166	46	96	0.945	165	28	116	1.307

PCA#

Component	Eigenvalue	% total variance	Cumul. %
PC1	1.64485	54.828	54.828
PC2	0.766946	25.565	80.393
PC3	0.588206	19.607	100.000

PCA weights#

	PC1
R	0.547638
G	-0.624166
B	-0.557234

PCA#

Component	Eigenvalue	% total variance	Cumul. %
PC1	1.5747	52.490	52.490
PC2	0.996565	33.219	85.709
PC3	0.42874	14.291	100.000

PCA weights#

	PC1
R	0.701533
G	-0.70581
B	-0.0984082

The values of the variables in the equation are standardized subtracting the mean and dividing by their standard deviations.

Mem2.5%. pH = 2.

[Hg(II)], mol/L	Camera: mobile Samsumg Galaxy				Camera: digital camera SONY DSC-W100			
	RGB parameters				RGB parameters			
	R	G	B	PC1[#]	G	G	B	PC1[#]
0	133	24	116	1.902	160	38	111	1.287
1×10^{-10}	140	23	117	2.006	169	42	115	1.803
1×10^{-9}	137	10	99	0.544	174	34	121	1.776
1×10^{-8}	145	14	105	1.171	180	15	88	0.524
1×10^{-7}	134	8	86	0.161	164	11	86	-0.167
1×10^{-6}	122	10	62	-0.384	158	13	96	-0.051
1×10^{-5}	114	8	20	-1.423	149	13	84	-0.526
1×10^{-4}	90	7	27	-1.995	134	9	36	-2.110
1×10^{-3}	82	9	33	-1.981	120	9	34	-2.536

PCA[#]

Component	Eigenvalue	% total variance	Cumul. %
PC1	2.42651	80.884	80.884
PC2	0.489328	16.311	97.194
PC3	0.0841669	2.806	100.000

PCA weights[#]

	PC1
R	0.571908
G	0.533094
B	0.623484

PCA[#]

Component	Eigenvalue	% total variance	Cumul. %
PC1	2.43336	81.112	81.112
PC2	0.487005	16.234	97.345
PC3	0.0796383	2.655	100.000

PCA weights[#]

	PC1
R	0.566919
G	0.537441
B	0.624307

[#] The values of the variables in the equation are standardized subtracting the mean and dividing by their standard deviations.

Mem2.5%. pH = 7.

[Hg(II)], mol/L	Camera: mobile Samsumg Galaxy				Camera: digital camera SONY DSC-W100			
	RGB parameters				RGB parameters			
	R	G	B	PC1[#]	G	G	B	PC1[#]
0	136	29	112	1.301	132	30	119	1.397
1×10^{-10}	144	28	122	1.539	140	28	121	1.488
1×10^{-9}	147	26	127	1.578	140	25	125	1.363
1×10^{-8}	148	27	128	1.647	147	27	129	1.698
1×10^{-7}	143	22	115	1.064	136	23	116	1.026
1×10^{-6}	110	9	36	-1.522	117	9	37	-1.294
1×10^{-5}	108	10	38	-1.489	111	10	37	-1.399
1×10^{-4}	99	8	34	-1.877	90	9	34	-2.012
1×10^{-3}	90	7	31	-2.240	83	8	32	-2.267

PCA[#]

Component	Eigenvalue	% total variance	Cumul. %
PC1	2.93316	97.772	97.772
PC2	0.0509873	1.700	99.471
PC3	0.0158574	0.529	100.000

PCA weights[#]

	PC1
R	0.576069
G	0.575185
B	0.580781

PCA[#]

Component	Eigenvalue	% total variance	Cumul. %
PC1	2.84758	94.919	94.919
PC2	0.133405	4.447	99.366
PC3	0.01901	0.634	100.000

PCA weights[#]

	PC1
R	0.565565
G	0.580433
B	0.585861

[#] The values of the variables in the equation are standardized subtracting the mean and dividing by their standard deviations.

Mem5%. pH = 2.

| [Hg(II)], mol/L | Camera: mobile Samsumg Galaxy | | | | Camera: digital camera SONY DSC-W100 | | | |
| | RGB parameters | | | | RGB parameters | | | |
	R	G	B	PC1[#]	G	G	B	PC1[#]
0	151	45	87	1.871	140	40	80	1.958
1×10^{-10}	161	44	84	1.981	146	37	77	1.889
1×10^{-9}	161	24	71	0.727	147	20	63	0.722
1×10^{-8}	167	25	72	0.982	154	20	63	0.861
1×10^{-7}	159	19	59	0.200	144	16	52	0.143
1×10^{-6}	146	19	40	-0.522	134	21	46	0.068
1×10^{-5}	141	21	13	-1.124	121	18	8	-1.191
1×10^{-4}	112	19	15	-1.896	92	11	8	-2.199
1×10^{-3}	103	15	17	-2.219	87	11	13	-2.251

PCA[#]

Component	Eigenvalue	% total variance	Cumul. %
PC1	2.37673	79.224	79.224
PC2	0.527017	17.567	96.791
PC3	0.0962575	3.209	100.000

PCA weights[#]

	PC1
R	0.556384
G	0.542551
B	0.629345

PCA[#]

Component	Eigenvalue	% total variance	Cumul. %
PC1	2.50172	83.391	83.391
PC2	0.410139	13.671	97.062
PC3	0.0881405	2.938	100.000

PCA weights[#]

	PC1
R	0.56498
G	0.550882
B	0.614269

[#] The values of the variables in the equation are standardized subtracting the mean and dividing by their standard deviations.

Mem5%. pH = 7.

| [Hg(II)], mol/L | Camera: mobile Samsumg Galaxy | | | | Camera: digital camera SONY DSC-W100 | | | |
| | RGB parameters | | | | RGB parameters | | | |
	R	G	B	PC1[#]	G	G	B	PC1[#]
0	158	51	89	1.573	147	44	79	1.503
1×10^{-10}	162	47	90	1.490	153	39	81	1.460
1×10^{-9}	167	44	92	1.545	159	40	85	1.685
1×10^{-8}	169	44	91	1.562	159	37	83	1.529
1×10^{-7}	163	38	78	0.952	154	31	70	0.893
1×10^{-6}	128	22	22	-1.534	119	19	18	-1.416
1×10^{-5}	124	22	24	-1.594	113	18	18	-1.569
1×10^{-4}	116	21	22	-1.878	103	16	15	-1.938
1×10^{-3}	107	20	22	-2.115	94	17	15	-2.147

PCA[#]

Component	Eigenvalue	% total variance	Cumul. %
PC1	2.91504	97.168	97.168
PC2	0.0733631	2.445	99.613
PC3	0.0115976	0.387	100.000

PCA weights[#]

	PC1
R	0.572709
G	0.576123
B	0.58317

PCA[#]

Component	Eigenvalue	% total variance	Cumul. %
PC1	2.89987	96.662	96.662
PC2	0.0872635	2.909	99.571
PC3	0.0128681	0.429	100.000

PCA weights[#]

	PC1
R	0.57234
G	0.575041
B	0.584599

[#] The values of the variables in the equation are standardized subtracting the mean and dividing by their standard deviations.

S11. **Hg(II) concentration *vs.* first component PC1 [principal component analysis of RGB parameters from digital pictures of sensory membranes dipped in water containing different concentrations of Hg(II)].**
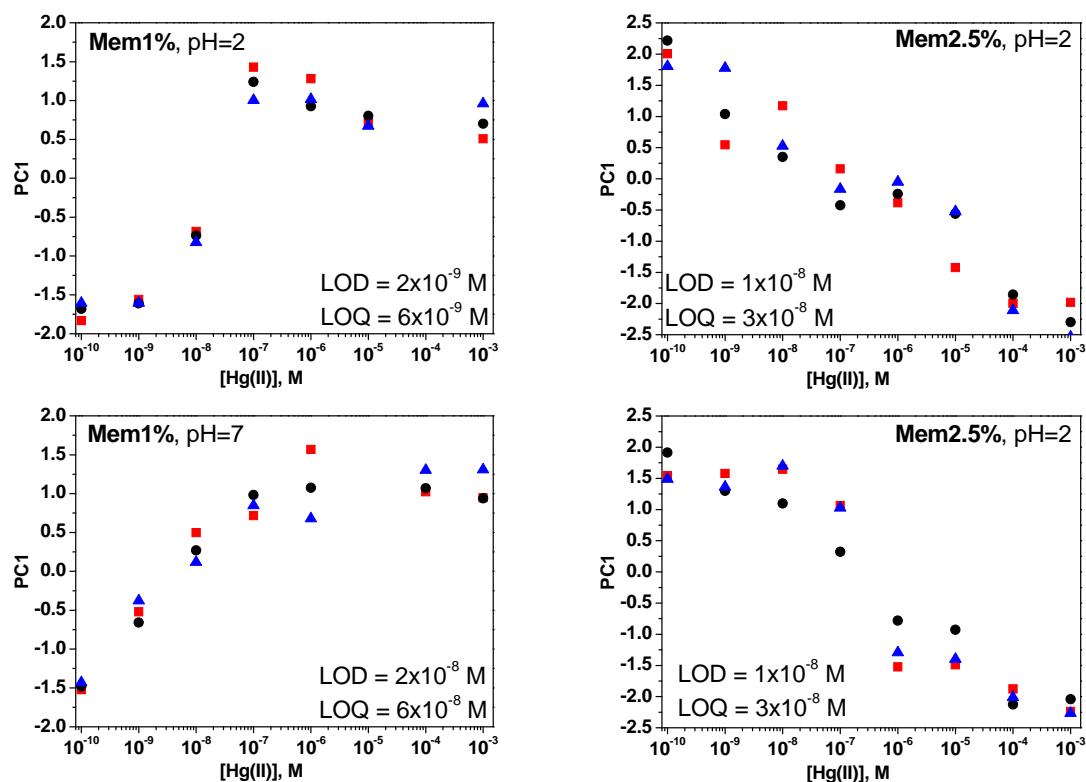

Fig. S5. Left: Mem1% strips. Right: Mem2.5% strips. Top: acidic media (pH=2, KCl-HCl). Bottom: neutral media (pH=7, TRIS-HCl). Digital pictures were taken with a Samsung Galaxy smartphone (■), a Kodak EasyShare DX4330 (●), and a Sony DSC-W100 (▲). The depicted LOD and LOQ were calculated using the results obtained PC1 components obtained with the Sony DSC-W100 (similar results were obtained using the other devices).

S12. **Principal component analysis (PCA) of the RGB data of pictures (SONY DSC-W100) of membrane strips of Mem1% after dipping in water at pH=2 in the presence of metal ions with a concentration of 1×10^{-5} M.**

Cation	RGB parameters			PC1[#]
	R	G	B	
Blank	178	106	146	-2.078
Hg(II)	198	4	152	0.554
Fe(III)	194	117	158	-1.945
Cr(VI)	199	108	162	-1.689
Cr(III)	202	134	170	-2.340
Cu(II)	196	87	172	-1.823
Ni(II)	219	104	178	-1.244
Fe(II)	216	122	178	-1.729
Zn(II)	197	120	166	-2.154

PC1 calculated using the standardization parameters and the PCA weights calculated for the titration of Hg(II) (S10 - **Mem1%**, digital camera SONY DSC-W100 -).

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