ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

The synthesis of switch-off fluorescent water-stable copper nanoclusters Hg²⁺ sensors *via* a simple one-pot approach by an *in situ* metal reduction strategy in the presence of a thiolated polymer ligand template.





Figure S1. A) ¹H-NMR spectra in CDCl₃ at 25 °C of the $p(MEO_2MA-co-AcSEMA)$ -x (Pn-X) samples. *Inset*: enlargement of signal 1 ($-SCOCH_3$). B) ¹H-NMR spectra in CDCl₃ at 25 °C of the $p(MEO_2MA-co-AcSEMA)$ -13% and $p(MEO_2MA-co-SEMA)$ -13% (P13-B) samples. C) FTIR-ATR spectra of $p(MEO_2MA-co-AcSEMA)$ -8% and $p(MEO_2MA-co-SEMA)$ -8% (P8-B) copolymers.

Table S1. Photophysical properties of hybrid CuNCs synthesized and functionalized with thiolated copolymers of p(MEO₂MA-*co*-SEMA) (P*n*-X).

Polymer ligand	Cu/polymer proportion [mM/mM]	λ _{em. max.} (nm)	% QYª	Time ^ь (day)
P2-C	0.5/2	533.3	0.8	2
P6-A	2/2	540.6	1.6	11
Р6-В	2/2	533.5	11.9	7
	2/1	537.5	7.9	1
	2/0.5	543.1	1.4	7
	1/1	538.4	4.7	2
	1.5/1	538.4	6.0	3
	0.5/2	535.5	5.6	7
P6-C	2/2	537.7	6.3	3
	2/1	536.0	5.3	1
	1.5/1	538.9	5.0	1
	1/1	540.5	4.7	1
P6-D	2/2	535.5	7.7	1
Р8-В	2/2	536.9	9.0	1
	2/1	535.8	3.6	2
	2/1.5	535.4	5.6	1
	2/0.5	568.0	0.7	1
	1/1	541.3	5.0	2
	1.5/1	536.4	6.2	1
P8-D	2/2	532.6	2.8	1
Р13-В	5/1	536.7	4.5	10
	2/2	535.9	4.4	4
	2/0.5	530.5	6.0	1
	2/1	539.9	4.9	6
	2/1.5	538.0	4.0	1
	2.5/0.5	558.3	1.9	4
	1/2	528.9	2.3	1
	1/1.5	527.9	2.3	1
	1/1	532.4	2.3	1
	1/0.2	554.0	1.6	4
	0.5/2	531.5	2.0	4

^aFluorescence quantum yield (% QY) (excitation at 400 nm) of the nanohybrids in dilute aqueous solutions relative to Rhodamine 6G dye in ethanol solution ($\Phi_F = 0.95$) [D. Magde *et al., Photochem. Photobiol.,* **2002,** *75*(4), 327-334]. ^bTime to reach the maximum emission quantum yield of fluorescence (QY).



Figure S2. Cloud points obtained by absorbance at 700 nm of water diluted solutions (1 mg.mL⁻¹) of hydrolyzed P6-B copolymer as a function of the pH of the medium.



Figure S3. A) FTIR-ATR spectra of P13-B copolymer once hydrolyzed and Cu@P13-B hybrid. B) sTEM images for Cu@P6-A and Cu@P6-D nanohybrids, as specified. (Note that sTEM samples were prepared from acid cold water solution). C) (i) High resolution XPS spectrum of Cu 2p electrons and (ii) Cu LMM Auger spectrum in the Cu@P6-B hybrid.



Figure S4. Maximum fluorescence quantum yield reached by Cu@P*n*-X nanohybrids in basic water solution at different molar proportions of the precursors (CuSO₄/P*n*-X mM/mM).



Figure S5. Evolution of fluorescence quantum yield of Cu@P13-B nanohybrids in basic water solution with the reaction time at different molar proportions of the precursors (CuSO₄/P13-B mM/mM). Photographs of the nanohybrid reactions at the different molar proportions of the precursors under UV lamp recorded on day 17 are included.



Figure S6. Evolution of fluorescence quantum yield relative to Rhodamine 6G dye in ethanol solution of A) Cu@P6-B, B) Cu@P8-B and C) Cu@P13-B nanohybrids in basic water solution with the days of reaction ($\lambda_{exc.}$ = 400 nm), Photographs of the nanohybrid reactions under Vis/UV lamp recorded after six months of storage are included.



Figure S7. Hydrodynamic size of the Cu@Pn-X nanohybrids obtained from Cu/polymer proportion of 2/2 mM with the thiolated copolymers (Pn-X) obtained by DLS measurements in diluted solutions (1 mg.mL⁻¹) below (10 °C-blue bars) and above (50 °C-red bars) the T_{cp} at different pHs: A) pH 6, B) pH 7 and C) pH 13. D) Z-potential values of the same hybrid solutions obtained at pH 13.



Figure S8. Cloud points obtained by absorbance at 700 nm and hydrodynamic size obtained by DLS of water diluted solutions (1mg.mL⁻¹) of A) Cu@P2-B, B) Cu@P6-B, C) Cu@P8-B and D) Cu@P13-B nanohybrids at different pHs.



Figure S9. A) Variation of integrated fluorescence emission of hybrid CuNCs (Cu@Pn-B) in the presence of different hydrogen peroxide (H₂O₂) concentrations as specified, after a minimum of 1 hour of incubation. B) Percentage of fluorescence emission decay as a function of irradiation time with UV-light (5 lamps, λ = 365nm, power= 34.2 W.m-2) of CuNCs@Pn-B [*Inset*: shows the fluorescence emission spectra evolution of Cu@P8-B nanohybrids with the irradiation time].



Figure S10. A) Selectivity of Cu@P8-B hybrids against different metal ions, measured by the change of their emission properties in the presence of 100 μ M concentration of each metal ion, as indicated. B) Fluorescence emission spectra obtained by the incubation of Cu@P8-B nanohybrids for a minimum of 1 hour in the presence of different metal ions at 100 μ M concentration as indicated ($\lambda_{exc.}$ = 400 nm).