

Supporting Information

Steady-state and time-resolved investigations on pyrene-based chemosensors

Javier Fernández-Lodeiro,¹ Cristina Núñez,² Catherine S. de Castro,³ Emilia Bértolo,⁴ J. Sérgio Seixas de Melo,^{3*} José Luis Capelo,^{1,2} Carlos Lodeiro^{1,2*}

¹Grupo BIOSCOPE, Departamento de Química, Faculdade de Ciências, Campus de Ourense, Universidade de Vigo, 32004 Vigo, Spain. Fax: +34 988 387001; E-mail: clodeiro@uvigo.es

²REQUIMTE/CQFB, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Monte de Caparica, Portugal. Fax: +351 212948550; Tel: +351 212948300; E-mail: cle@fct.unl.pt

³Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal. E-mail: sseixas@ci.uc.pt

⁴Ecology Research Group, Department of Geographical and Life Sciences, Canterbury Christ Church University. Canterbury, Kent. CT1 1QU. United Kingdom.

Synthesis details

Synthesis. Probes **P** and **L** were synthesized following a one-pot reaction, by direct condensation between the commercial carbonyl precursor 1-pyrene-carboxaldehyde and 2-methoxyaniline (**P**) or 1,5-bis(2-aminophenoxy)-3-oxopentane (**L**).ⁱ The final products **P** and **L** were isolated as an air-stable yellow and red solid, with *ca.* 89 and 81% yield, respectively. Both probes have been characterized by microanalysis, melting points, IR, ¹H and ¹³C NMR, UV-Vis and fluorescence emission spectroscopy and MALDI-TOF-mass spectrometry.

Elemental analysis of **P** and **L** confirmed the purity of the probes. The infrared spectrum (in KBr) shows bands at 1649 and 1647 cm⁻¹ respectively, corresponding to the imine bond $\nu(\text{C}=\text{N})$, and no peaks attributable to unreacted amine or carbonyl groups were present. The matrix assisted laser desorption time-of-flight mass (MALDI-TOF-MS) spectra of **P** and **L**, obtained irradiating the samples at 337 nm by a N₂ laser, show parent peaks at 336.21 [**PH**]⁺ and 713.11 [**LH**]⁺ m/z, respectively.

The ¹H and ¹³C NMR spectra of compounds **P** and **L** were recorded using DMSO-*d*⁶ as solvent. Proton signals were identified using standard 2D homonuclear (COSY) and ¹H/¹³C heteronuclear (HMQC) spectra. The ¹H NMR spectra of **P** and **L** in DMSO-*d*⁶ show peaks at *ca.* 8.87 and 9.58, respectively, corresponding to the imine protons. In the ¹H NMR spectrum, the aromatic hydrogen atoms were observed as multiple signals in the aromatic, and the protons of the ethylene bridges appeared as triplets in the aliphatic region.

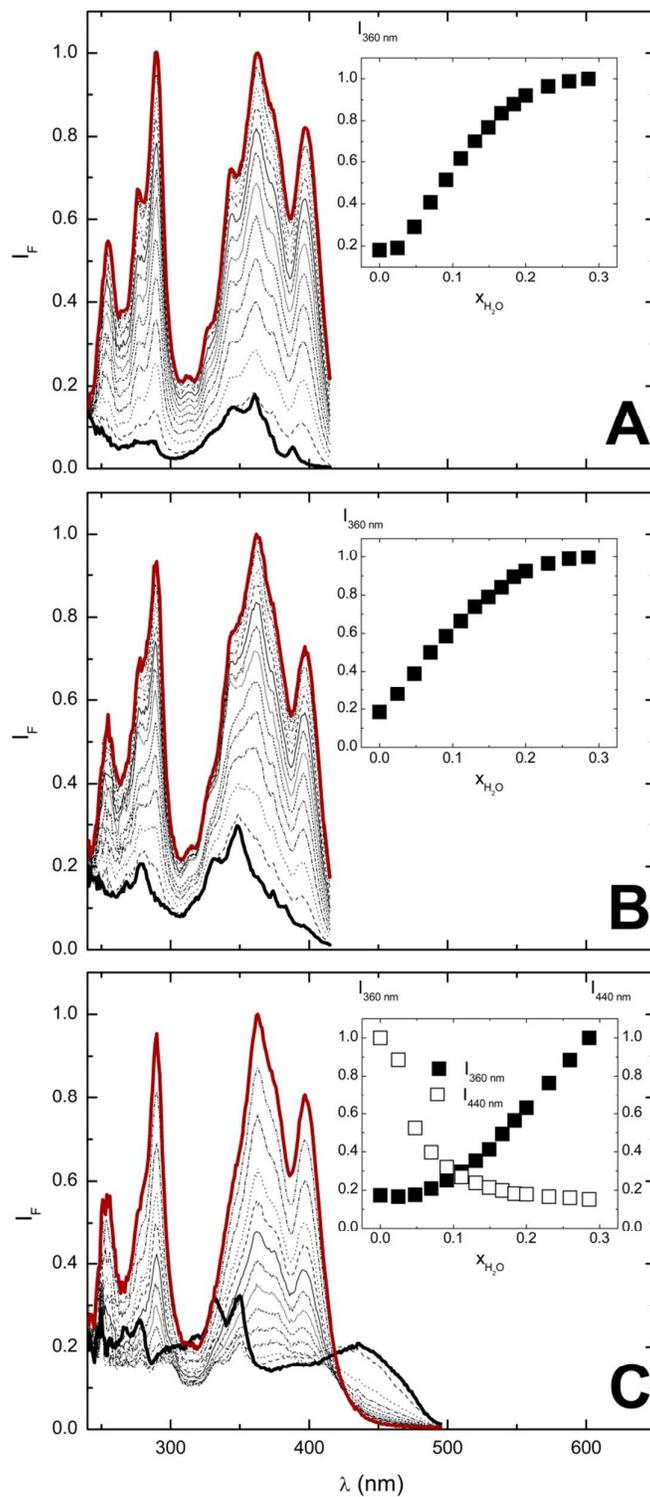


Figure S1. Fluorescence excitation titrations of chemosensor (A) P and (B and C) L collected at 420 nm and 500 nm (from top to bottom) as a function of increasing amounts of water in dioxane. The insets show the fluorescence

intensities at 360 nm for excitation spectra collected at 420 nm, and fluorescence intensities at 360 nm and 440 nm for excitation spectra collected at 500 nm. ($[P] = [L] = 5.00 \times 10^{-6} \text{ M}$, $\lambda_{emP} = 420 \text{ nm}$, $\lambda_{em1(L)} = 420 \text{ nm}$ and $\lambda_{em2(L)} = 500 \text{ nm}$). The bold dark line is for $x_{H_2O} = 0$ whereas the bold red line is for $x_{H_2O} = 0.29$.

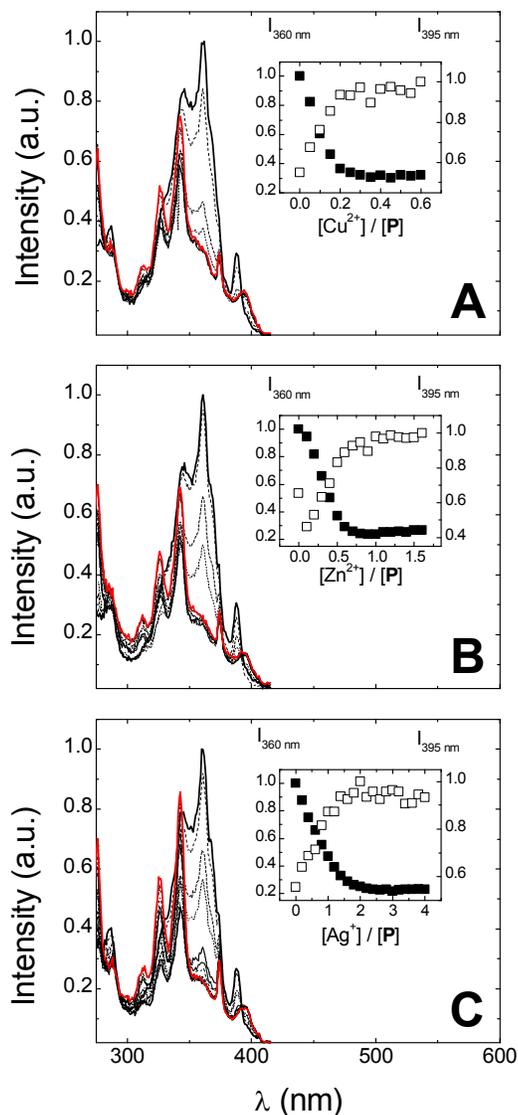


Figure S2. Fluorescence excitation titrations of chemosensor **P** collected at 420 nm as a function of increasing amounts of (A) $Cu(BF_4)_2$, (B) $Zn(BF_4)_2$ and (C) $Ag(BF_4)$ in dioxane. The insets show the fluorescence intensities at 360 and

395 nm, ($[P] = 5.00 \times 10^{-6}$ M, $\lambda_{em1} = 420$ nm). The bold dark line is for $[Cu^{2+}] / [P] = [Zn^{2+}] / [P] = [Ag^+] / [P] = 0$ whereas the bold red line is for $[Cu^{2+}] / [P] = 0.6$, $[Zn^{2+}] / [P] = 1.6$ and $[Ag^+] / [P] = 4$, respectively.

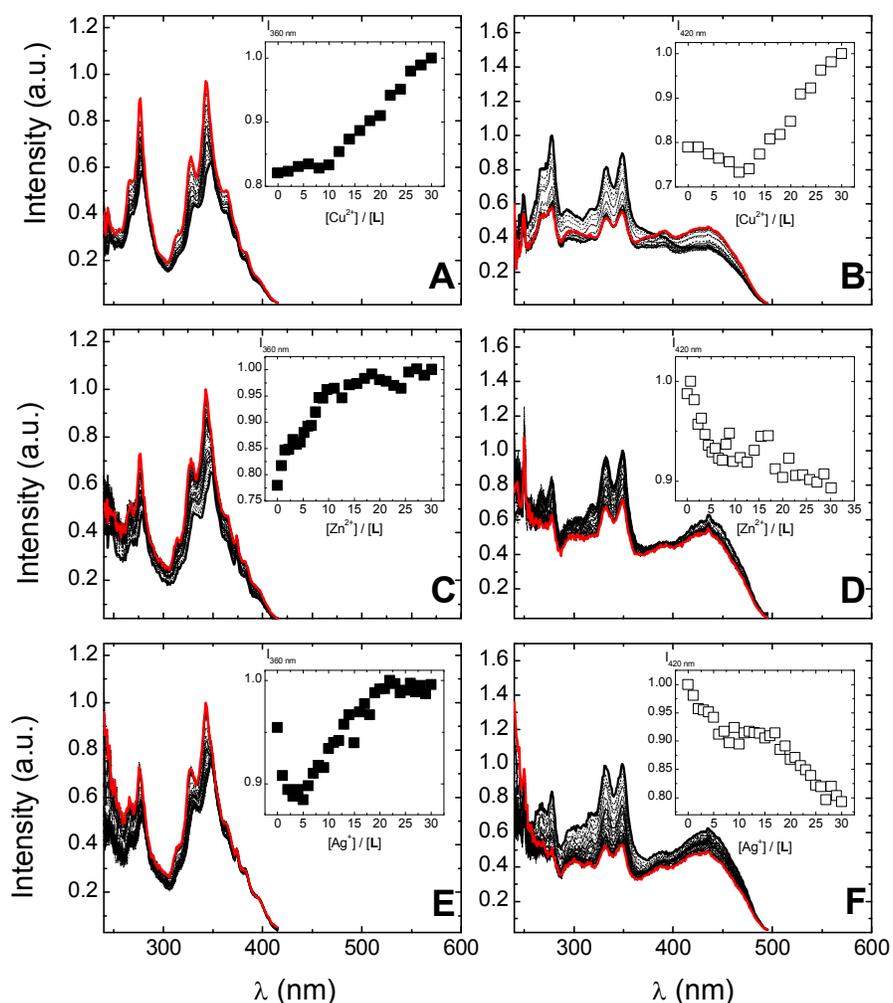


Figure S3. Fluorescence excitation titrations of chemosensor **L** collected at 420 nm (left panels) and 500 nm (right panels) as a function of increasing amounts of (A and B) $Cu(BF_4)_2$, (C and D) $Zn(BF_4)_2$ and (E and F) $Ag(BF_4)$ in dioxane. The insets show the fluorescence intensities at 360 nm for excitation spectra collected at 420 nm, and at 420 nm for excitation spectra collected at 500 nm

($[L] = 5.00 \times 10^{-6} \text{ M}$, $\lambda_{em1} = 420 \text{ nm}$ and $\lambda_{em2} = 500 \text{ nm}$). The bold dark line is for $[Cu^{2+}] / [L] = [Zn^{2+}] / [L] = [Ag^+] / [L] = 0$ whereas the bold red line is for $[Cu^{2+}] / [L] = [Zn^{2+}] / [L] = [Ag^+] / [L] = 30$.

The absorption and emission spectra of **L** in (black) pure dioxane, (red) in $x_{H_2O} = 0.80$ in dioxane and (grey) after the removal of water are presented in Figure S4.

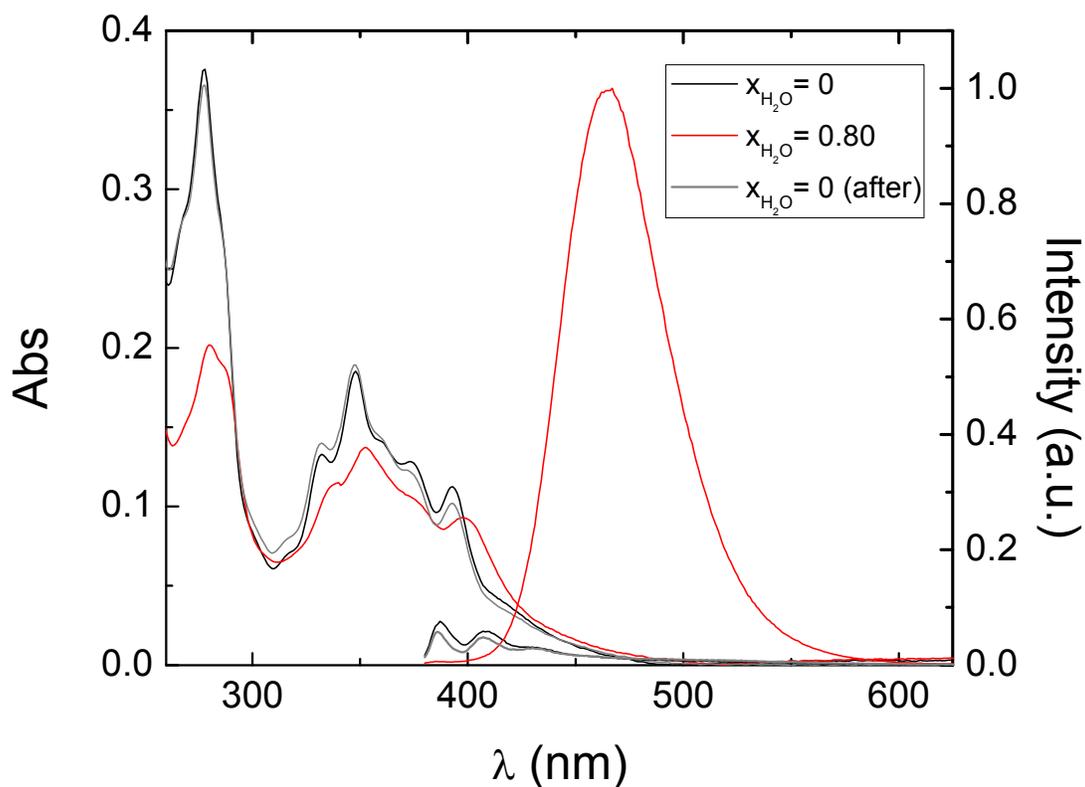


Figure S4. Absorption and emission spectra of **L**: (black) in pure dioxane, (red) in $x_{H_2O} = 0.80$ in dioxane and (grey) in pure dioxane after the removal of water from solution (B).

ⁱ (a) Vicente, M.; Lodeiro, C.; Adams, H.; Bastida, R.; de Blas, A.; Fenton, D. E.; Macías, A.; Rodríguez, A.; Rodríguez-Blas, T. *Eur. J. Inorg. Chem.* **2000**, *6*, 1015. (b) Lodeiro, C.; Bastida, R.; de Blas, A.; Fenton, D. E.; Macías, A.; Rodríguez, A., Rodríguez-Blas, T. *Inorg. Chim. Acta* **1998**, *267*, 55.