Supporting Information for

## Photochemical functionalisation of optical nanotips with a rhodamine chemosensor for remote through-fiber detection of Hg<sup>2+</sup>

Kun Chen,<sup>*a*</sup> Catherine Adam,<sup>*b*</sup> Neso Sojic,<sup>\*,*b*</sup> and Michael Schmittel<sup>\*,*a*</sup>

<sup>a</sup> Center of Micro- and Nanochemistry and Engineering, Universität Siegen, Organische Chemie I, Adolf-Reichwein-Strasse 2, D-57068 Siegen, Germany

<sup>b</sup>Groupe Nanosystèmes Analytiques, Institut des Sciences Moléculaires, CNRS UMR 5255, Université Bordeaux 1, ENSCPB, 16 avenue Pey-Berland, 33607 Pessac, France.

## Table of content

pH effect on photoluminescence of rhodamine 4	Page 2
Absorption spectra of rhodamine 4 in presence of different cations	Page 2
Time response of rhodamine <b>4</b> toward $Hg^{2+}$	Page 2
PL titration of rhodamine 4 with $Hg^{2+}$ in MeCN/ 0.1 M HEPES buffer	Page 3
Job plot of rhodamine <b>4</b> with Hg <sup>2+</sup>	Page 3
NMR spectra of compound 4 and $[4 + Hg^{2+}]$	Page 3
Absorption spectra of glass slide functionalised with compound 10 after irradiation	Page 4
In situ spectrum of the functionalised optical fiber bundles in presence of $Hg^{2+}$	Page 4
Titration curve of luminescence intensity fiber vs. lg [Hg <sup>2+</sup> ]	Page 5



Fig. S1 PL intensity (at  $\lambda_{em} = 556$  nm) of rhodamine 4 (10  $\mu$ M) in MeCN/buffer (95/5, v/v) from pH 1 to 13 ( $\lambda_{ex} = 520$  nm).



Fig. S2 UV-Vis absorption spectra of rhodamine 4 (10  $\mu$ M) in presence of different cations in buffer solution (MeCN / 0.1 M HEPES buffer (pH = 7.40 ± 0.10) solution = 95:5, v/v).



Fig. S3 Time response of rhodamine 4 (10  $\mu$ M) toward Hg<sup>2+</sup> (0.2 mM) in buffer solution (MeCN / 0.1 M HEPES buffer (pH = 7.40  $\pm$  0.10) solution = 95:5, v/v) monitored by PL at  $\lambda_{em}$  = 556 nm ( $\lambda_{ex}$  = 520 nm).



**Fig. S4** PL titration (at  $\lambda_{em} = 556$  nm,  $\lambda_{ex} = 520$  nm) of rhodamine 4 (10 µM) in presence of different amounts of Hg<sup>2+</sup> in aqueous buffer solution (MeCN / 0.1 M HEPES buffer (pH = 7.40 ± 0.10) = 50:50, v/v).



**Fig. S5** Job plot of compound 4 vs. Hg<sup>2+</sup> in MeCN with  $[Hg^{2+}] + [4] = 10 \ \mu\text{M}$  followed by PL (at  $\lambda_{em} = 556 \text{ nm}$ ,  $\lambda_{ex} = 520 \text{ nm}$ ).



Fig. S6 <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) spectra of (a) 4, (b) 4 + Hg<sup>2+</sup>. Dichloromethane is indicated by  $\mathbf{\nabla}$ .



Fig. S7 UV-Vis absorption spectra of the surface-immobilised compound 10 on the glass slide after irradiation with the LC8 system for different periods of time in methanol.



Fig. S8 The *in-situ* PL spectrum ( $\lambda_{ex} = 514 \text{ nm}$ ) of the rhodamine-functionalised optical fiber bundles in presence of Hg<sup>2+</sup> (5 mM) in MeCN / 0.1 M HEPES buffer (pH = 7.40 ± 0.10) = 95:5, v/v.



**Fig. S9** Photoluminescence titration ( $\lambda_{em} = 558 \text{ nm}$ ,  $\lambda_{ex} = 514 \text{ nm}$ ) of rhodamine-functionalised fiber bundles *vs.* lg [Hg<sup>2+</sup>] in MeCN / 0.1 M HEPES buffer solution (pH = 7.40 ± 0.10) = 95:5, v/v.