Preparation, photophysical, electrochemical and sensing properties of luminescent tetrazine-doped silica nanoparticles

Jérémy Malinge, Clémence Allain, Laurent Galmiche, Fabien Miomandre and Pierre Audebert

PPSM, ENS Cachan, CNRS UMR8531, 61 av President Wilson, F-94230 Cachan, France

Figure S1. Size distribution of silica nanoparticles prior to functionalization measured by DLS (left) and by TEM images (right)
<i>Figure S2.</i> Fluorescence profile evolution during the grafting reaction (left) and graphical sketch $Imax = f(t)$ (right)
Figure S3. UV-Vis extinction spectra of tetrazine 2 in acetonitrile (dotted line) and of a suspension of NP1 in acetonitrile (plain line)
Figure S4. Emission spectra of dye 2 in the presence of increasing pollutant concentration (0-1.6mM) in acetonitrile. Conditions: $[dye] = 0.29 \text{ mM}$, $\lambda exc = 340 \text{ nm}$
Figure S5. Emission spectra of NP1 in the presence of increasing pollutant concentration (0-1.6mM) in acetonitrile. Conditions: $[dye] = 0.29 \text{ mM}, \lambda exc = 340 \text{ nm}.$ 4
Figure S6. Emission spectra of NP2 in the presence of increasing pollutant concentration (0-1.6mM) in acetonitrile. Conditions: $[dye] = 0.29 \text{ mM}$, $\lambda exc = 340 \text{ nm}$
Figure S7. Evolution of the fluorescence decay upon addition of EtOA (0-1.51mM) to a suspension of NP1. Conditions $[Tz]=0.21 \text{ mM}, \lambda_{exc} = 340 \text{ nm}.$ 5
<i>Figure S8.</i> Average fluorescence lifetime calculation methodology



Figure S1. Size distribution of silica nanoparticles prior to functionalization measured by DLS (left) and by TEM images (right)



Figure S2. Fluorescence profile evolution during the grafting reaction (left) and graphical sketch Imax = f(t) (right)



Figure S3. UV-Vis extinction spectra of tetrazine 2 in acetonitrile (dotted line) and of a suspension of NP1 in acetonitrile (plain line).



Figure S4. Emission spectra of dye **2** in the presence of increasing pollutant concentration (0-1.6mM) in acetonitrile. Conditions: [dye] = 0.29 mM, $\lambda exc = 340 \text{ nm}$.



Figure S5. Emission spectra of NP1 in the presence of increasing pollutant concentration (0-1.6mM) in acetonitrile. Conditions: [dye] = 0.29 mM, $\lambda exc = 340 \text{ nm}$.



Figure S6. Emission spectra of NP2 in the presence of increasing pollutant concentration (0-1.6mM) in acetonitrile. Conditions: [dye] = 0.29 mM, $\lambda exc = 340 \text{ nm}$.



Figure S7. Evolution of the fluorescence decay upon addition of EtOA (0-1.51mM) to a suspension of NP1. Conditions [Tz]=0.21 mM, $\lambda_{exc} = 340$ nm.

The average fluorescence lifetime represents the average amount of time a fluorophore remains in its excited state. In the case of monoexponential decays, the average decay is equal to the fluorescence lifetime. This is the case for dyes **2** and **4**. In the case of complex systems such as doped nanoparticles, the average excited state lifetime was calculated with a numerical approach (eq. A) thanks to the fitted curved of the fluorescence decay:

$$<\tau>=rac{\sum_{i}a_{i} au_{i}}{\sum_{i}a_{i}}$$
 (eq. A)

where a_i is the pre exponential term and τ_i the discrete lifetime

Figure S8. Average fluorescence lifetime calculation methodology