## Supplementary Information



Figure S1. Normalized absorption (continuous line) and excitation spectra ( $\lambda_{\mathrm{em}}=655 \mathrm{~nm}$, dashed red line) of a (PDDA/PSS/PDDA/TPPS) ESAM.


Figure S2. Absorption spectra of (PDDA/TPPS/PDDA/PSS)n (a) and (PDDA/TPPS-PSS 1:100)n films (b) after the deposition of a TPPS layer.


Figure S3. Absorption spectra of TPPS in aqueous solution ( $\mathrm{c}=1.9 \times 10^{-6} \mathrm{M}$ ) at $\mathrm{pH}=8.0$ (continuous line) and upon interaction with mercury(II) ions (dashed line). Mercury(II) ion concentration was $6.6 \times 10^{-6} \mathrm{M}$.


Figure S4. Fluorescence emission spectra of TPPS ( $\mathrm{c}=1.3 \times 10^{-7} \mathrm{M}$ ) in aqueous solution at $\mathrm{pH}=8.0$
(continuous line) and after addition of mercury(II) ions (dashed line). Mercury(II) ion concentration was 4.3 $\mathrm{x} 10^{-6} \mathrm{M} . \lambda \mathrm{ex}=416 \mathrm{~nm}$.


Figure S5. AFM image ( $5 \times 5 \mu \mathrm{~m}$ ) of a PDDA/TPPS film (on the left) and the corresponding threedimensional representation (on the right).


Figure S6. Fluorescence microscopy image $(125 \times 125 \mu \mathrm{~m})$ of a ((PDDA/PSS $)_{\times 2} /$ PDDA/TPPS $)$.


Figure S7. Adsorption kinetics of mercury(II) ions, at four different initial concentrations, on (PDDA/PSS/PDDA/TPPS) ESAM at $25^{\circ} \mathrm{C}$ in borate buffer at $\mathrm{pH}=8.0$ : linear fit to the pseudo-second-order equation is reported. The initial mercury(II) ion concentrations were: $3.3 \cdot 10^{-5} \mathrm{M}(\boldsymbol{\bullet}), 3.3 \cdot 10^{-6} \mathrm{M}(\bullet), 6.7 \cdot 10^{-7}$ $\mathrm{M}(\mathbf{\Delta}), 3.3 \cdot 10^{-7} \mathrm{M}(\boldsymbol{*})$.

Table S1. Slope and intercept values obtained from the linear fit of experimental data of adsorption to the kinetic pseudo-second-order equation (eq. 2 b ) as a function of $\left[\mathrm{Hg}^{2+}\right]_{0}$; the values of the fractional surface coverage at equilibrium $\theta_{(\mathrm{eq})}$ are reported.

| $\left[\mathrm{Hg}^{2+}\right]_{0}(\mathrm{~mol} / \mathrm{L})$ | $\frac{1}{\theta_{(\mathrm{eq})}}$ | $\frac{1}{\mathrm{k}_{2} \cdot \mathrm{~N}_{(\mathrm{eq})} \cdot \theta_{(\mathrm{eq})}}$ (min) | $\theta_{(\mathrm{eq})}$ | $\mathrm{R}^{2}$ |
| :---: | :---: | :---: | :---: | :---: |
| $3.3 \times 10^{-5}$ | 0.97 | 6.47 | 1.03 | 0.999 |
| $3.3 \times 10^{-6}$ | 1.33 | 20.92 | 0.75 | 0.995 |
| $6.7 \times 10^{-7}$ | 1.63 | 30.20 | 0.61 | 0.996 |
| $3.3 \times 10^{-7}$ | 2.43 | 31.17 | 0.41 | 0.998 |

