Supplementary Materials

Naphthalimide-piperazine derivatives as multifunctional "on" and "off" fluorescent switches for pH, Hg^{2+} and Cu^{2+} ions

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Figure S1. Absorbance spectra of: a) **NI-1** and c) **NI-2** in a buffer/methanol mixture (2:1) at different pH; plot of absorbance ratio at 388 nm and 410 nm vs. pH for: b) **NI-1** and d) **NI-2**.

Figure S2. a) Fluorescence spectra of **NI-2** in buffer methanol mixture (2:1) at different pH; b) fluorescence intensity at 525 nm vs. pH.

Figure S3. NI-1 in the presence of metal ions (from left: blank, Zn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Hg^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Ag^{+}, Mn^{2+}, Ba^{2+}, Cd^{2+}, Mg^{2+}, Ca^{2+}) c (metal ion) = 3.0×10^{-5} M.

Figure S4. UV-Vis spectra of **NI-1** solution upon the addition of 20 equiv. of a) Hg(II) and b) Cu(II) ions.

Figure S5. Changes in the emission spectra of **NI-1** upon gradual addition of Cu^{2+} and EDTA.

Figure S6. Changes in the emission spectra of **NI-1** upon gradual addition of Hg^{2+} and EDTA.

Figure S7. Benesi-Hildebrand's plot in linear range for **NI-1** binding with a) Cu^{2+} b) Hg^{2+}.

Figure S8. Dependence of fluorescence intensity of **NI-1** (5.00×10^{-7} M) in MeOH / buffer pH 5.5 (v / v, 1/2) at 523 nm on the ion concentration in the linear range of dependence for a) Cu^{2+} b) Hg^{2+} ion.

Figure S9. Stern-Volmer plot of the ratio of the fluorescence intensities (F_0/F) of **NI-1** against the increasing concentration of a) Cu^{2+} and b) Hg^{2+} ions in linear range.

Figure S10. UV-Vis spectra of **NI-2** upon the addition of Hg(II) ions.

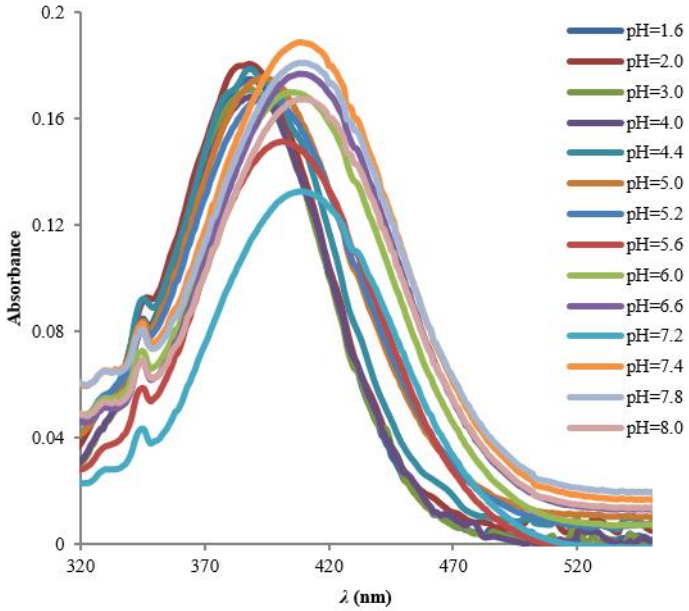
Figure S11. Job's plot fluorescence intensity at 525 nm on the molar content of **NI-2** in presence of Hg^{2+} ions at a total concentration of 5.00×10^{-6} M. The extrapolated directions of intensity dependence on the molar fraction of **NI-2** are presented.

Figure S12. Benesi-Hildebrand's plot in linear range for **NI-2** binding with Hg^{2+}.

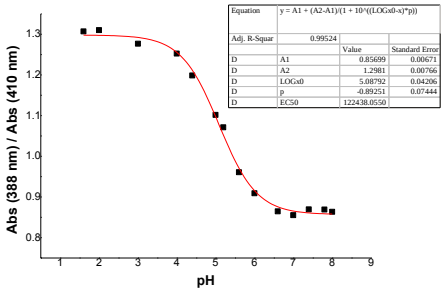
Figure S13. Dependence of fluorescence intensity of **NI-2** (6.53×10^{-6} M) in MeOH / buffer 5.5 (v/v, 1/2) at 525 nm on the ion concentration in the linear range of dependence for Hg^{2+} ion.

Figure S14. Reversibility test for **NI-2** and Hg(II) binding.

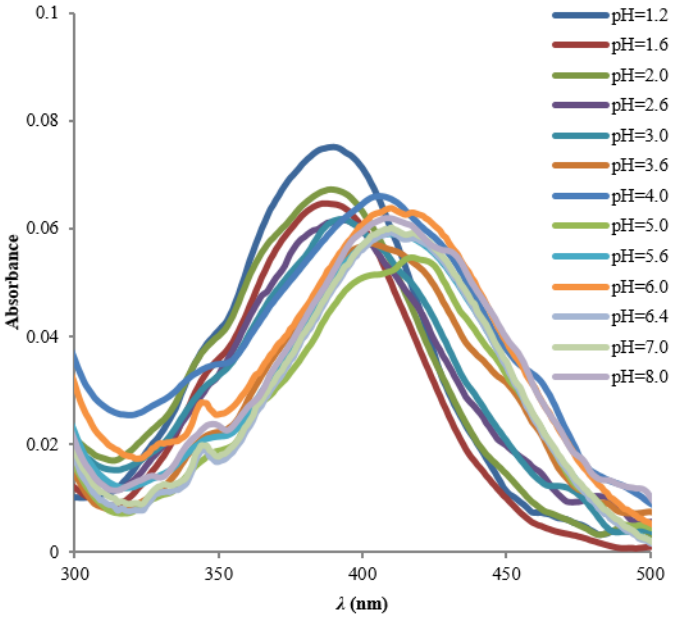
a)


Absorbance
λ (nm)
pH=1.6
pH=2.0
pH=3.0
pH=4.0
pH=4.4
pH=5.0
pH=5.2
pH=5.6
pH=6.0
pH=6.6
pH=7.2
pH=7.4
pH=7.8
pH=8.0

b)


Abs (388 nm) / Abs (410 nm)
pH
Equation y = A1 + (A2-A1)/(1 + 10^((LOGx0-x)*p))
Adj. R-Squar 0.99524
Value Standard Error
D A1 0.85699 0.00671
D A2 1.2981 0.00766
D LOGx0 5.08792 0.04206
D p -0.89251 0.07444
D EC50 122438.0550

c)


Absorbance
λ (nm)
pH=1.2
pH=1.6
pH=2.0
pH=2.6
pH=3.0
pH=3.6
pH=4.0
pH=5.0
pH=5.6
pH=6.0
pH=6.4
pH=7.0
pH=8.0

d)

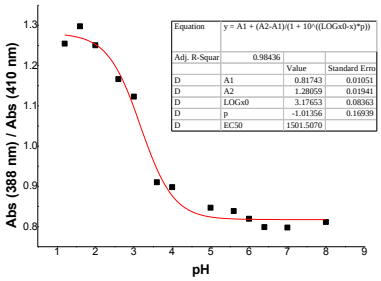
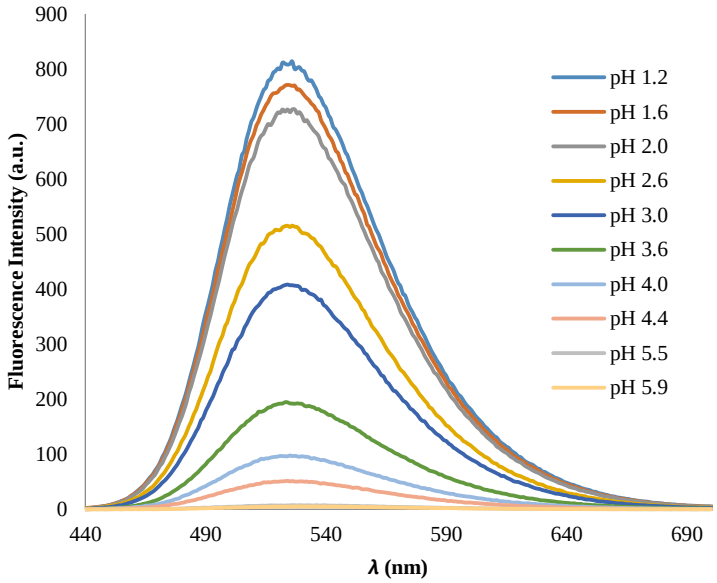

Abs (388 nm) / Abs (410 nm)
pH
Equation y = A1 + (A2-A1)/(1 + 10^((LOGx0-x)*p))
Adj. R-Squar 0.98436
Value Standard Error
D A1 0.81743 0.01051
D A2 1.28059 0.01941
D LOGx0 3.17653 0.08363
D p -1.01356 0.16939
D EC50 1501.5070

Figure S1. Absorbance spectra of: a) **NI-1** and c) **NI-2** in a buffer/methanol mixture (2:1) at different pH; plot of absorbance ratio at 388 nm and 410 nm vs. pH for: b) **NI-1** and d) **NI-2**. The spectra of compounds **NI-1** and **NI-2** were recorded in MeOH/buffer (1:2) at compound concentrations 6.56×10^{-5} M and 6.54×10^{-5} M, respectively.



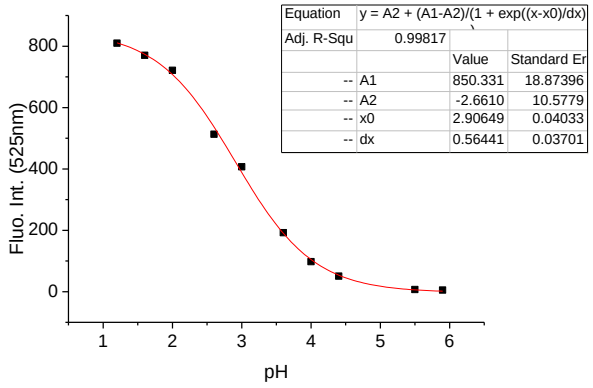


Figure S2. a) Fluorescence spectra of **NI-2** in buffer methanol mixture (2:1) at different pH; b) fluorescence intensity at 525 nm vs. pH.

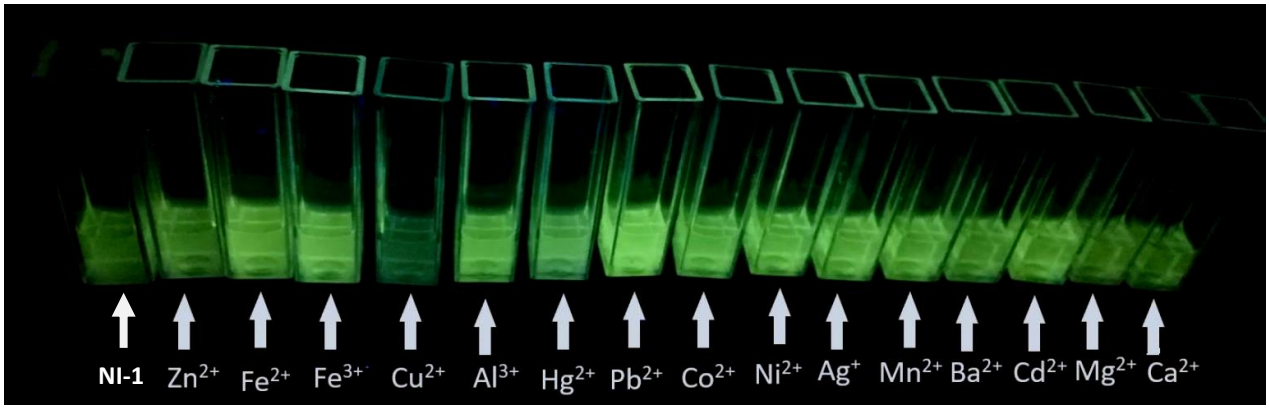


Figure S3. NI-1 in the presence of metal ions (from left: blank, Zn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Hg^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Ag^{+}, Mn^{2+}, Ba^{2+}, Cd^{2+}, Mg^{2+}, Ca^{2+}) *c* (metal ion) = 3.0×10^{-5} M.

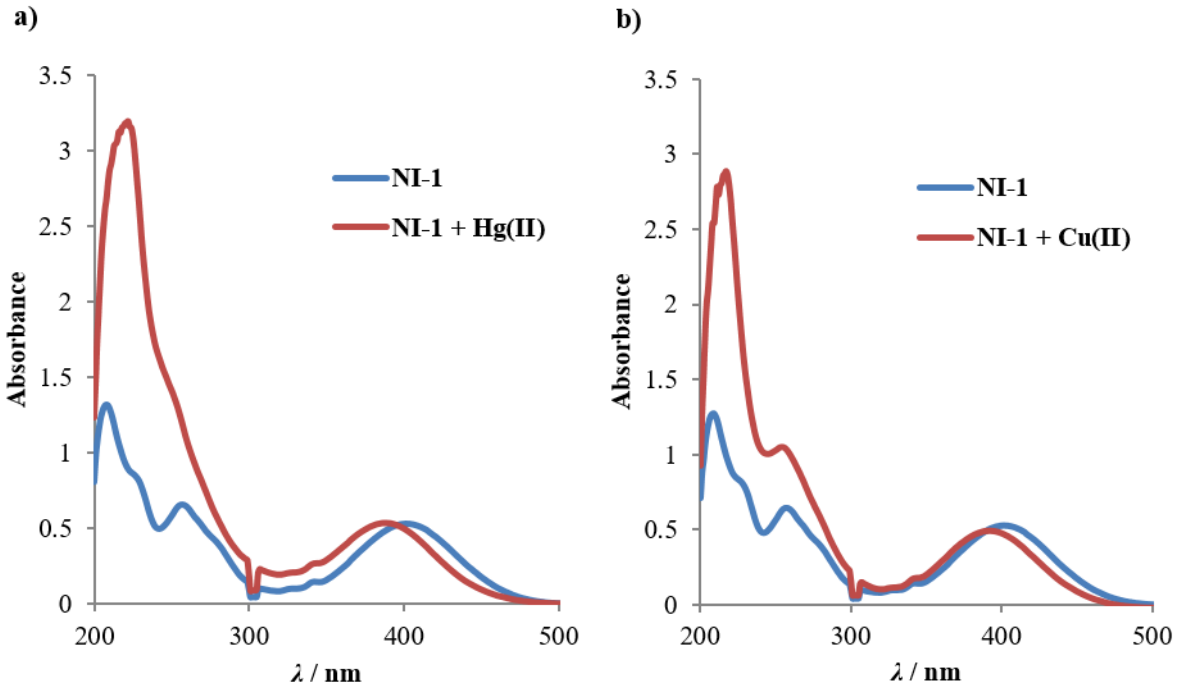


Figure S4. UV-Vis spectra of **NI-1** solution upon the addition of 20 equiv. of a) Hg(II) and b) Cu(II) ions.

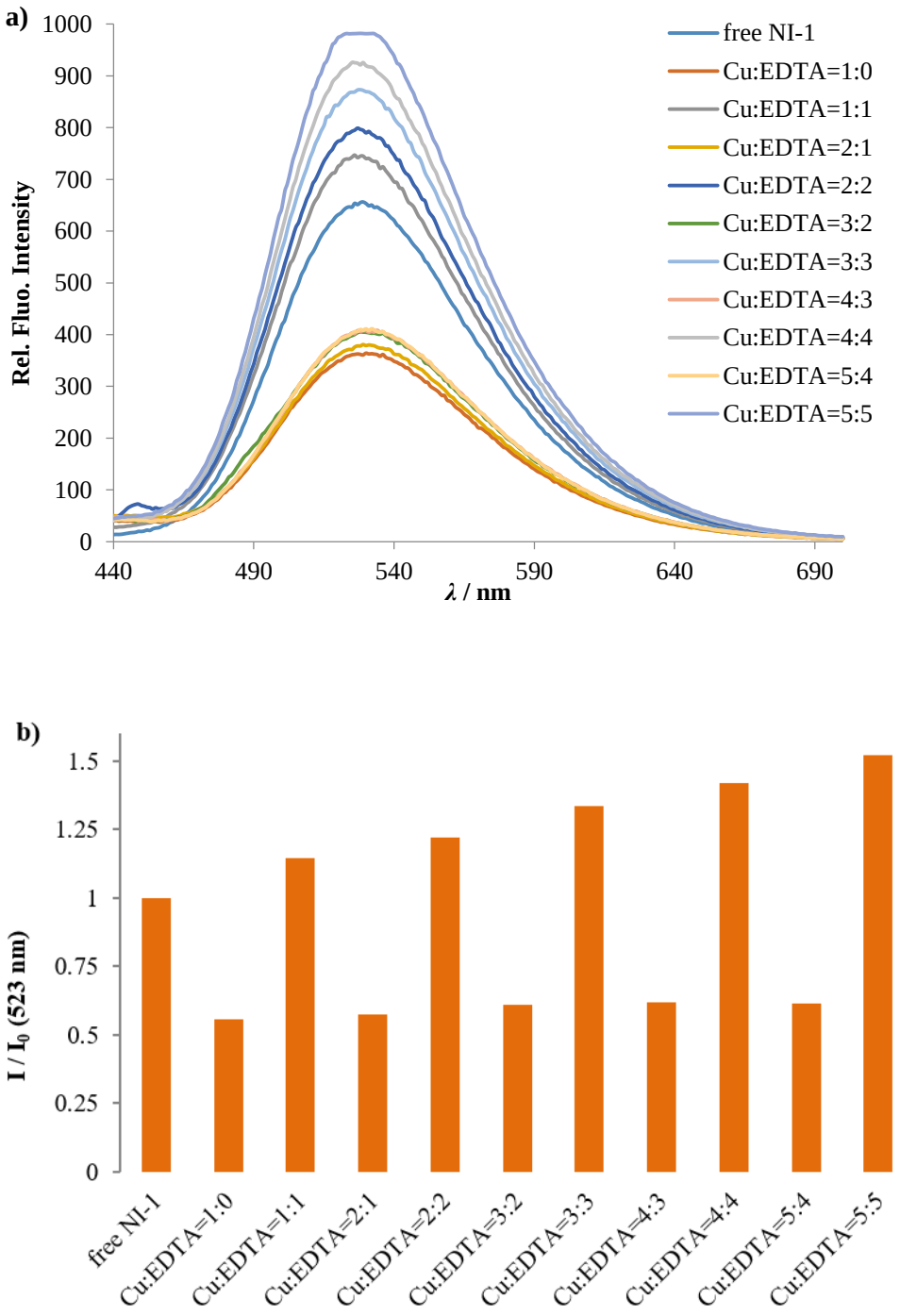


Figure S5. Changes in the emission spectra of **NI-1** upon gradual addition of Cu^{2+} and EDTA.

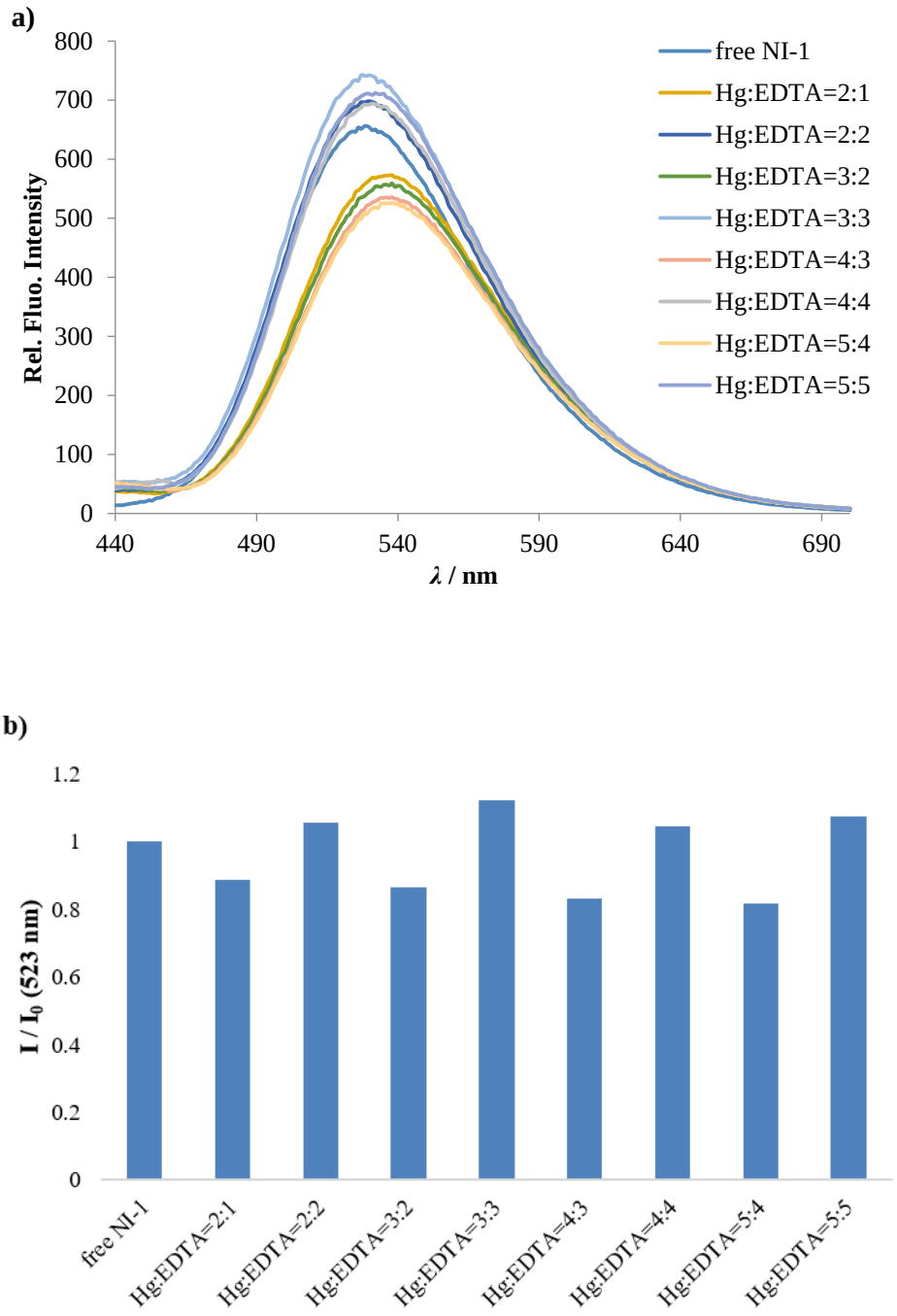


Figure S6. Changes in the emission spectra of **NI-1** upon gradual addition of Hg^{2+} and EDTA.

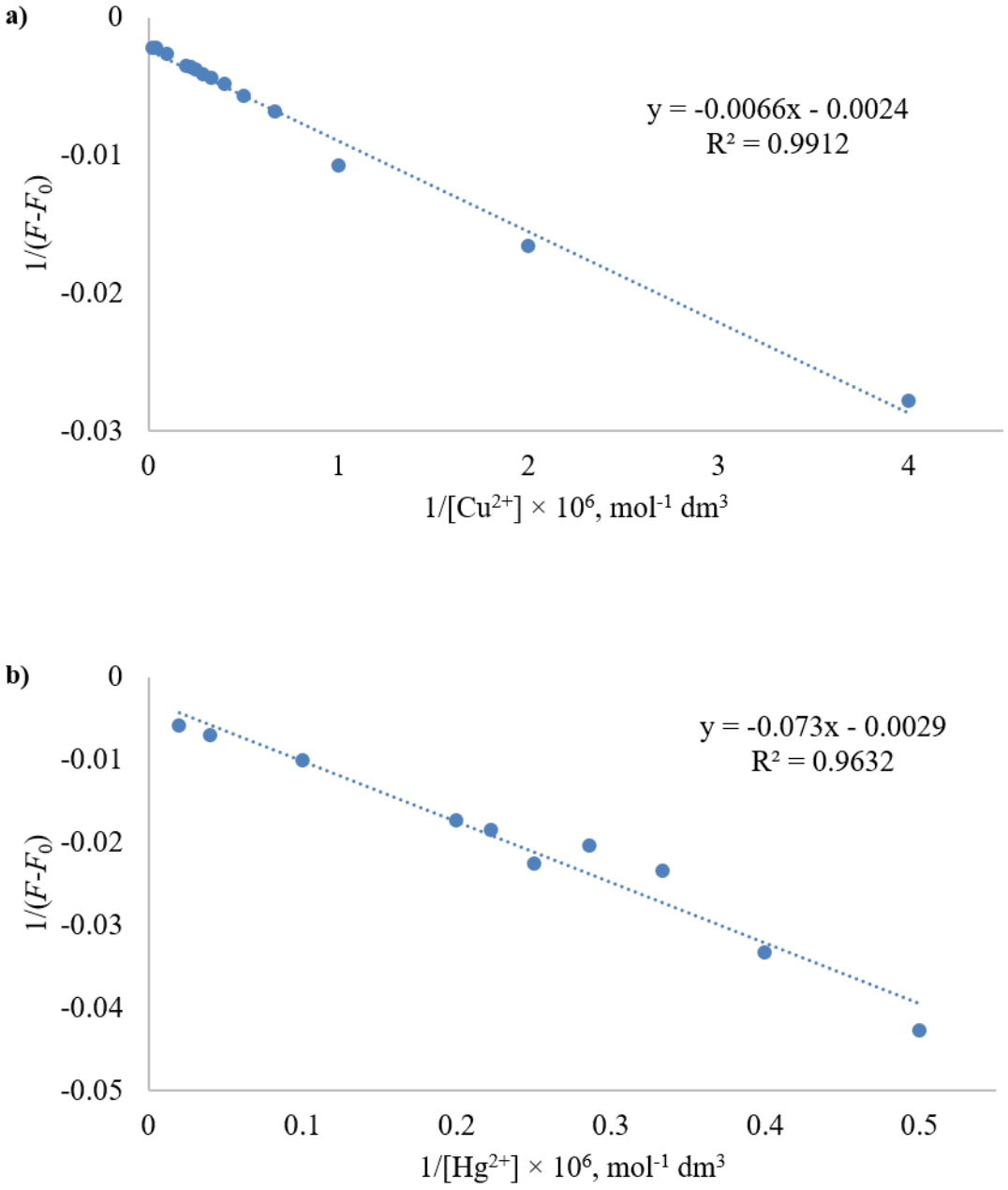


Figure S7. Benesi-Hildebrand's plot in linear range for **NI-1** binding with a) Cu^{2+} b) Hg^{2+}.

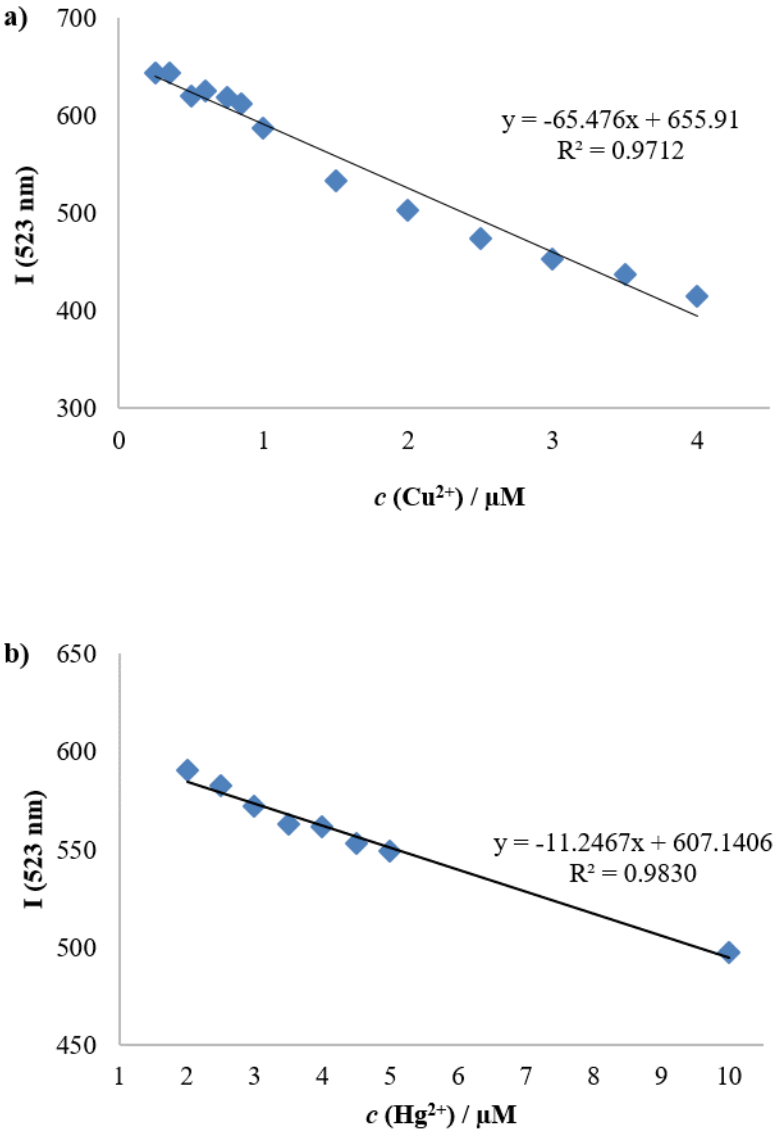


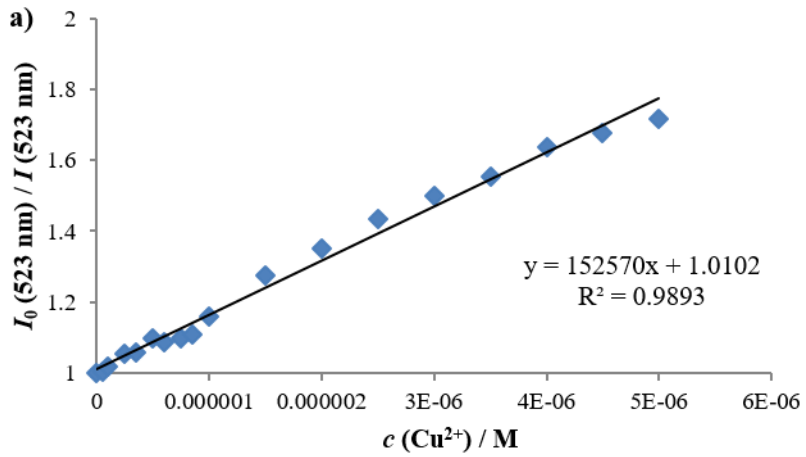
Figure S8. Dependence of fluorescence intensity of **NI-1** (5.00×10^{-7} M) in MeOH / buffer pH 5.5 (v / v, 1/2) at 523 nm on the ion concentration in the linear range of dependence for a) Cu^{2+} b) Hg^{2+} ion.

Stern-Volmer's equation for **NI-1** was derived using:

$$\frac{F_0}{F} = 1 + K_{sv}[Q]$$

where F_0 - initial fluorescence intensity, F – fluorescence intensity in the presence of the analyte, $[Q]$ – concentration of fluorescence quencher (Cu^{2+} or Hg^{2+} ion), K_{sv} – Stern-Volmer constant.

The Stern-Volmer constant is equal to the slope in the linear range of the fluorescence intensity ratio of **NI-1** without metal ions and fluorescence intensity in the presence of ions at 523 nm as shown in Fig. S10. For Cu^{2+} ion the Stern-Volmer constant is 152570 M^{-1}, and for Hg^{2+} ion it is 23909 M^{-1}.



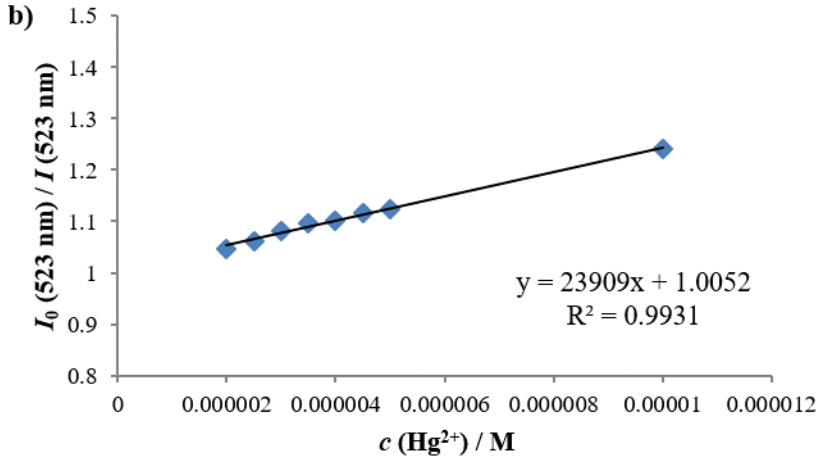


Figure S9. Stern-Volmer plot of the ratio of the fluorescence intensities (F_0/F) of **NI-1** against the increasing concentration of a) Cu^{2+} and b) Hg^{2+} ions in linear range.

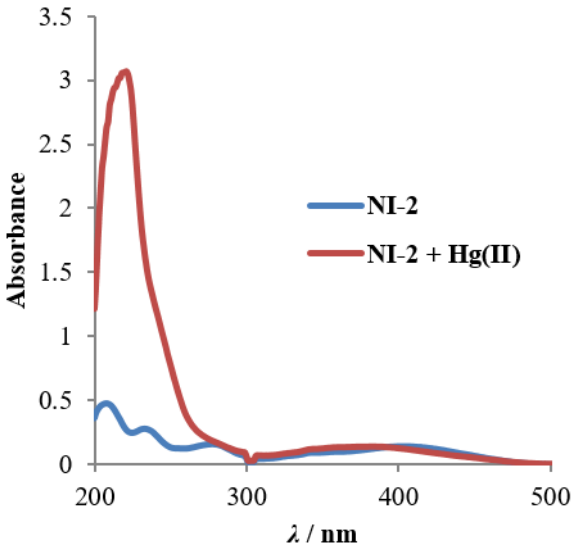


Figure S10. UV-Vis spectra of **NI-2** upon the addition of Hg(II) ions.

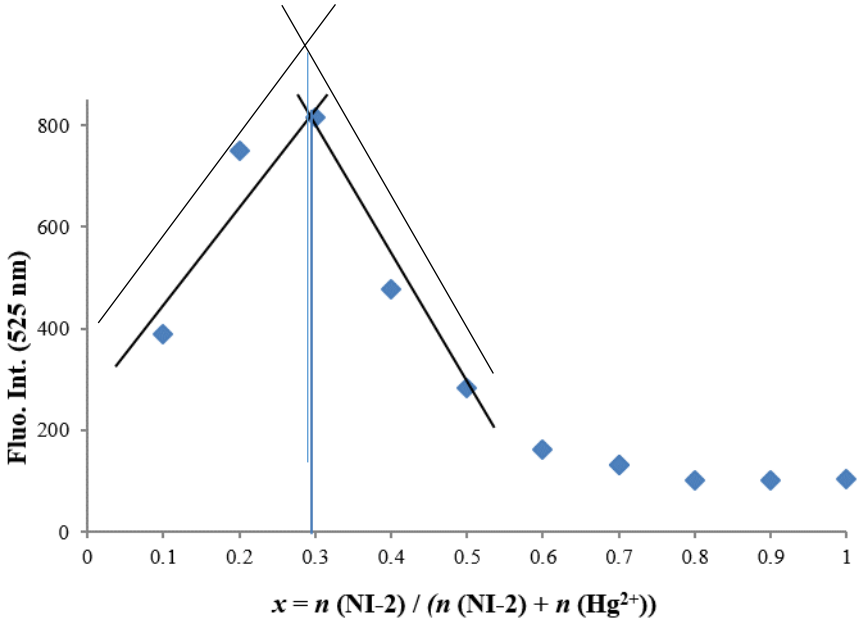


Figure S11. Job's plot fluorescence intensity at 525 nm on the molar content of **NI-2** in presence of Hg^{2+} ions at a total concentration of 5.00×10^{-6} M. The extrapolated directions of intensity dependence on the molar fraction of **NI-2** are presented.

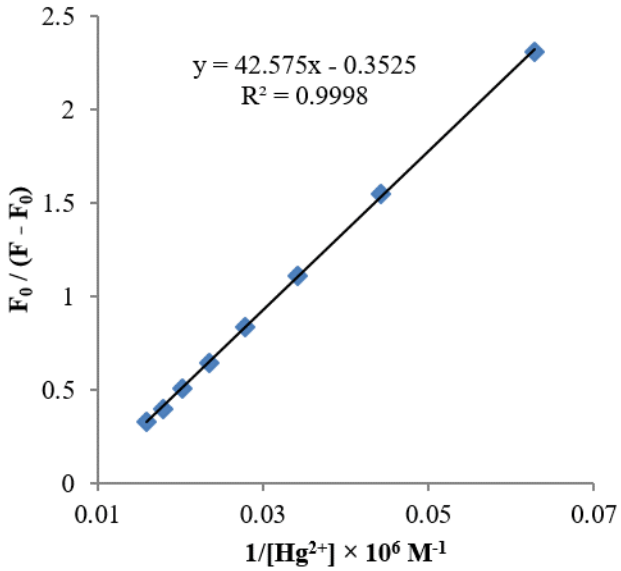


Figure S12. Benesi-Hildebrand's plot in linear range for **NI-2** binding with Hg^{2+}.

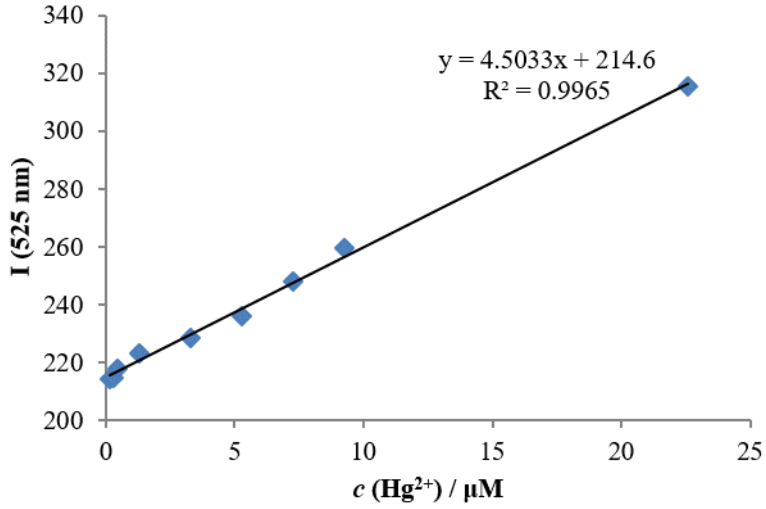


Figure S13. Dependence of fluorescence intensity of **NI-2** (6.53×10^{-6} M) in MeOH / buffer 5.5 (v/v, 1/2) at 525 nm on the ion concentration in the linear range of dependence for Hg^{2+} ion.

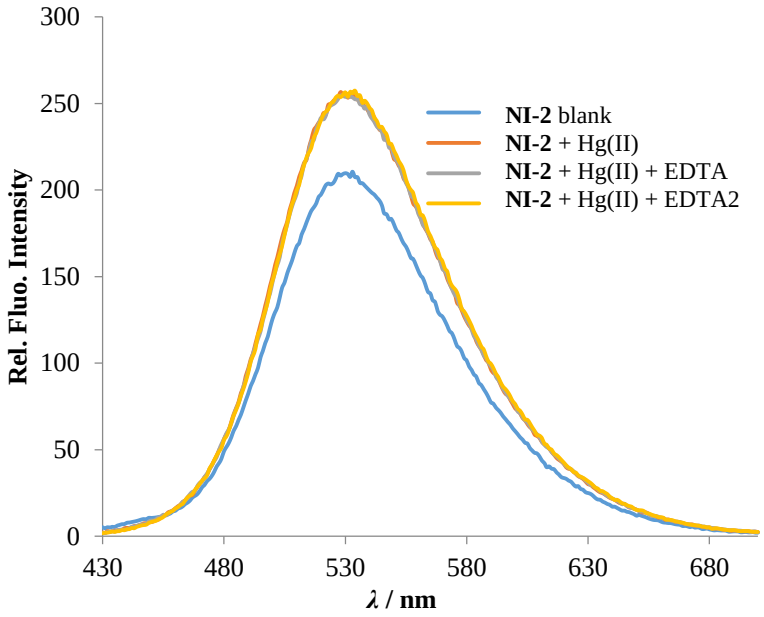


Figure S14. Reversibility test for **NI-2** and Hg(II) binding.