

Supporting Information

Chemically reversible binding of H₂S to a zinc porphyrin complex: towards implementation of a reversible sensor via a “coordinative-based approach”.

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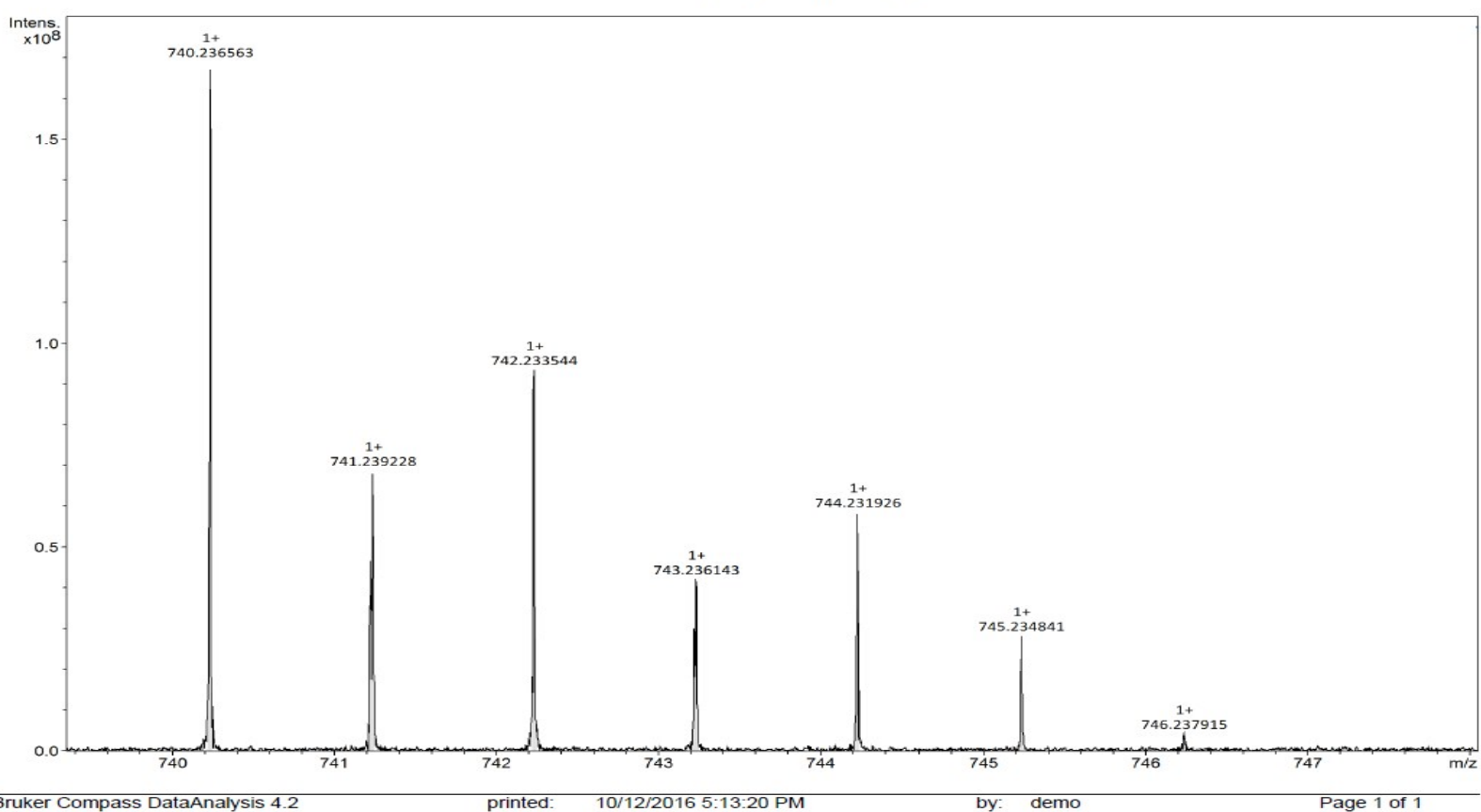


Figure S1. HR MALDI-FT-ICR spectrum of *TMPyPZn* in water solution (ionizing the sample in the positive ion mode)

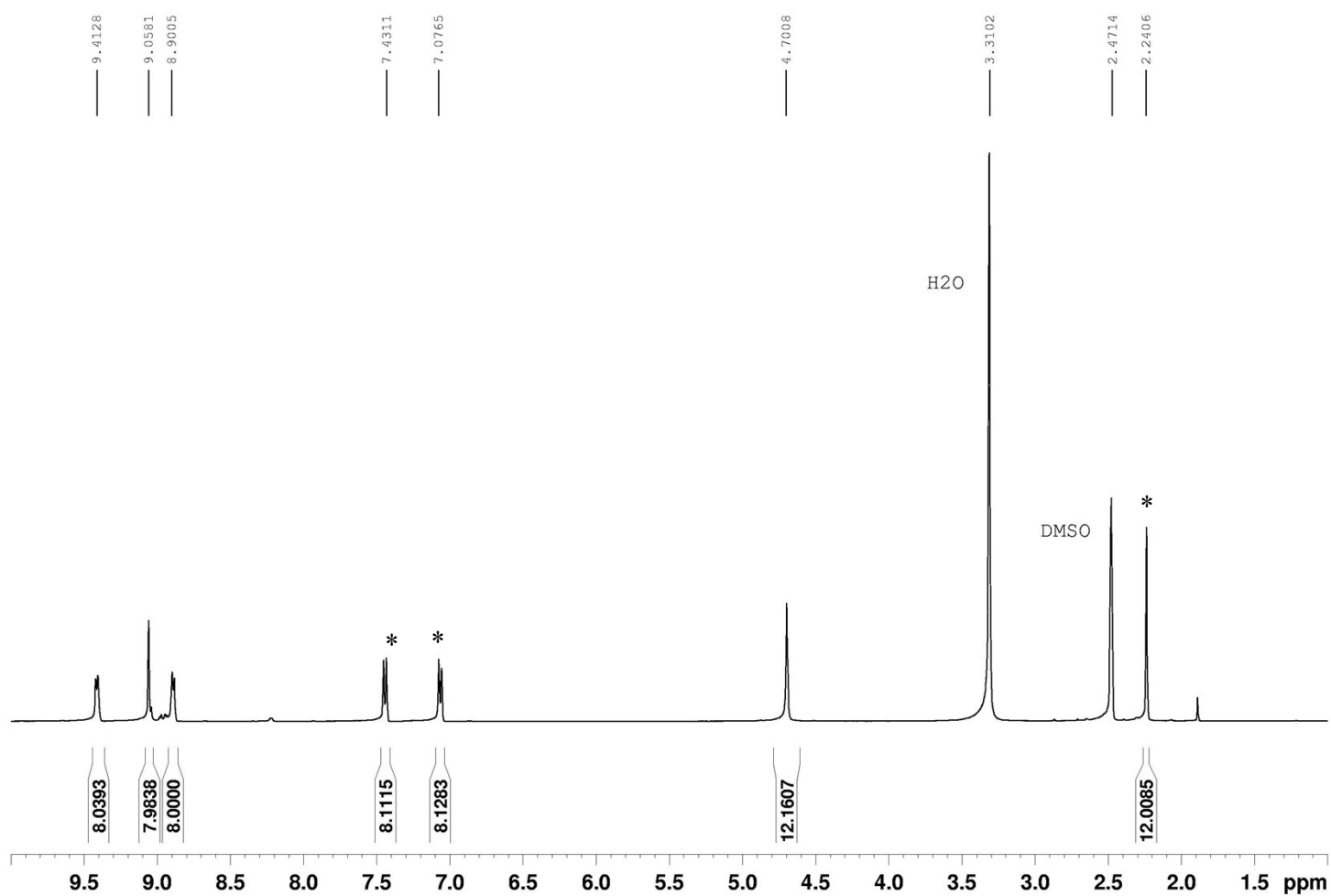


Figure S2. ¹H NMR spectrum of *TMPyPZn* in DMSO-*d*₆ (rt, 400.13 MHz). Peaks denoted with a (*) correspond to the toluenesulfonate counterion.

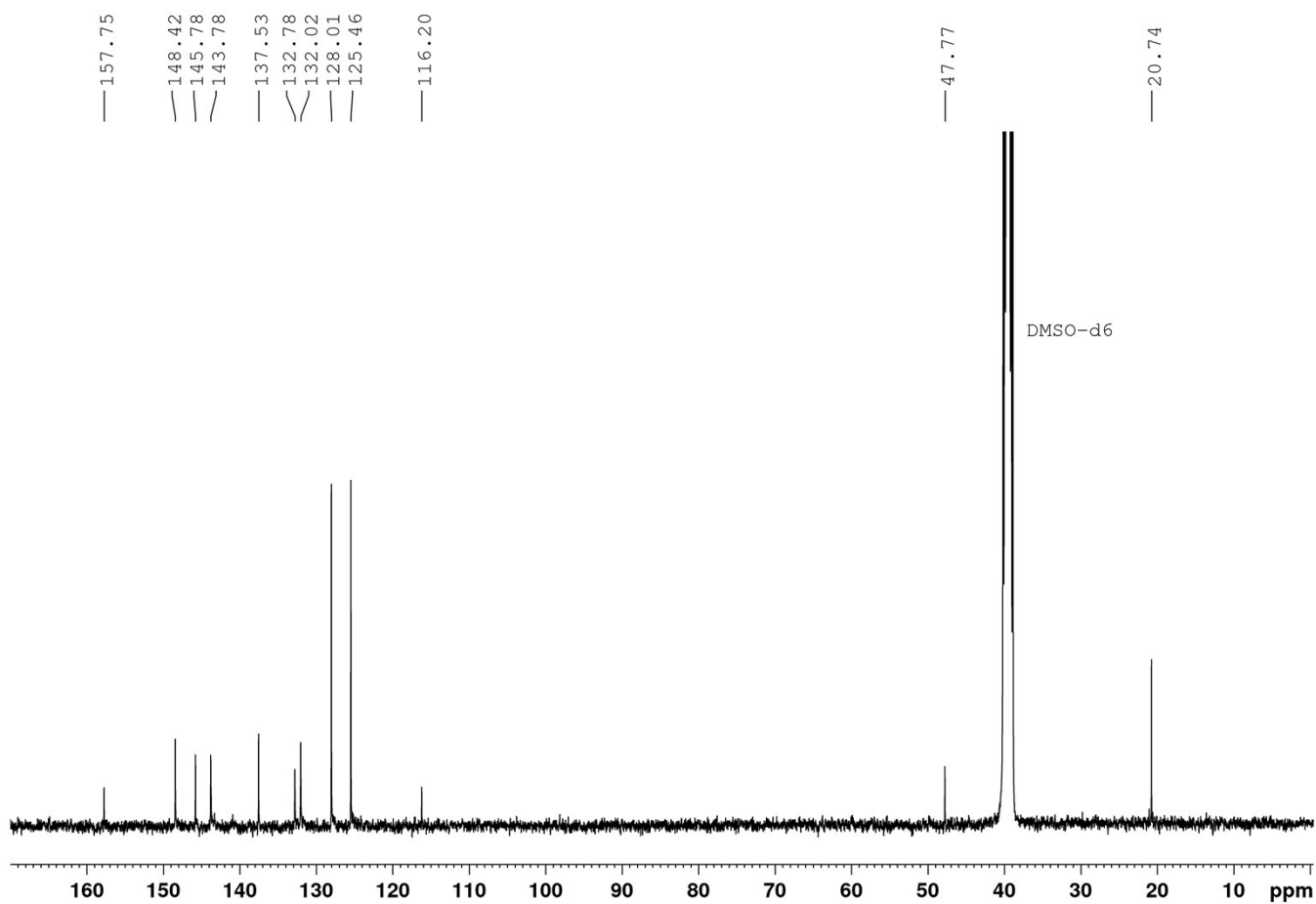


Figure S3. ^{13}C NMR spectrum of *TMPyPZn* in $\text{DMSO-}d_6$ (rt, 400.13 MHz)

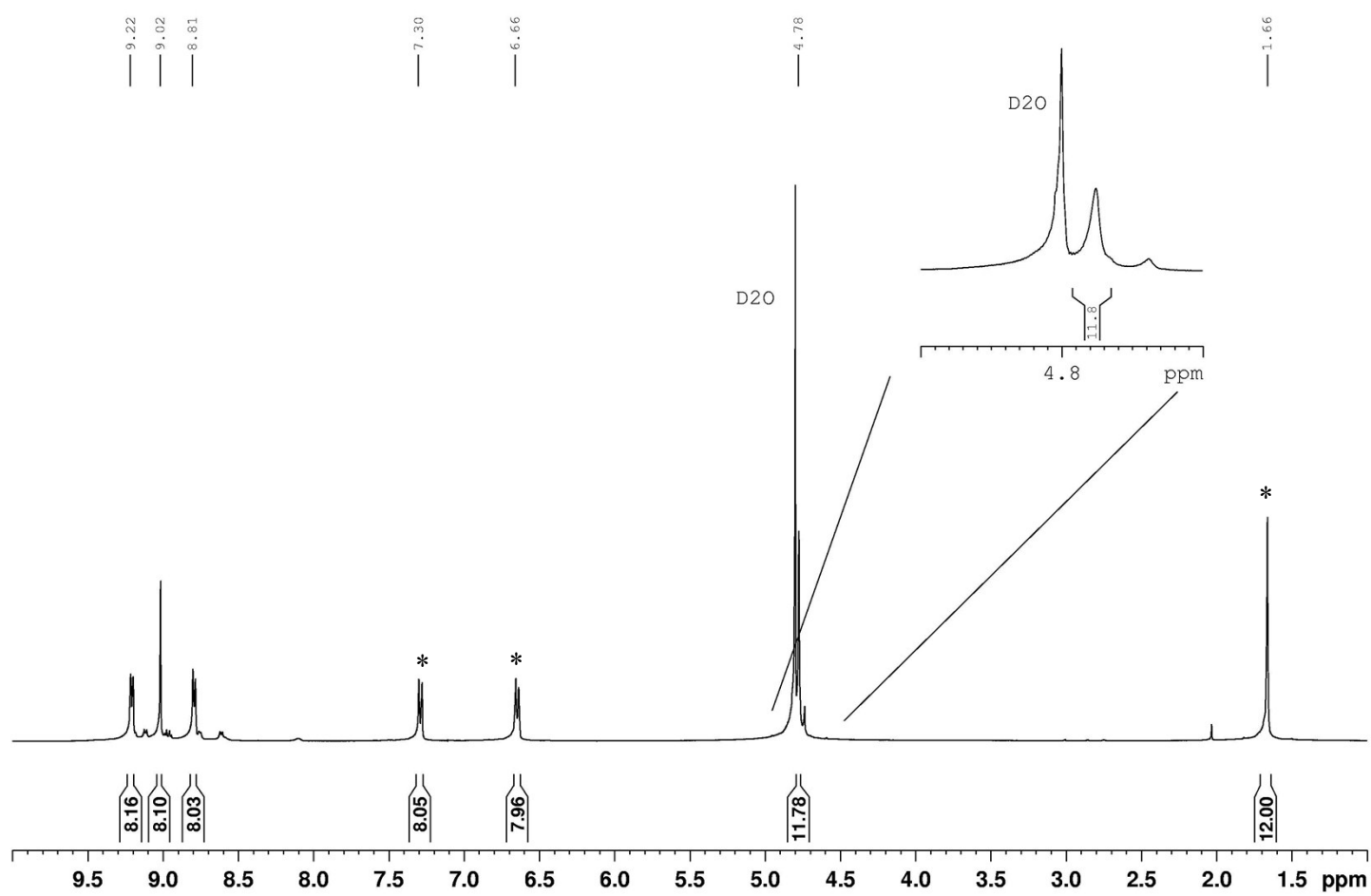


Figure S4. ^1H NMR spectrum of *TMPyPZn* in D_2O (rt, 400.13 MHz). Peaks denoted with a (*) correspond to the toluenesulfonate counterion.

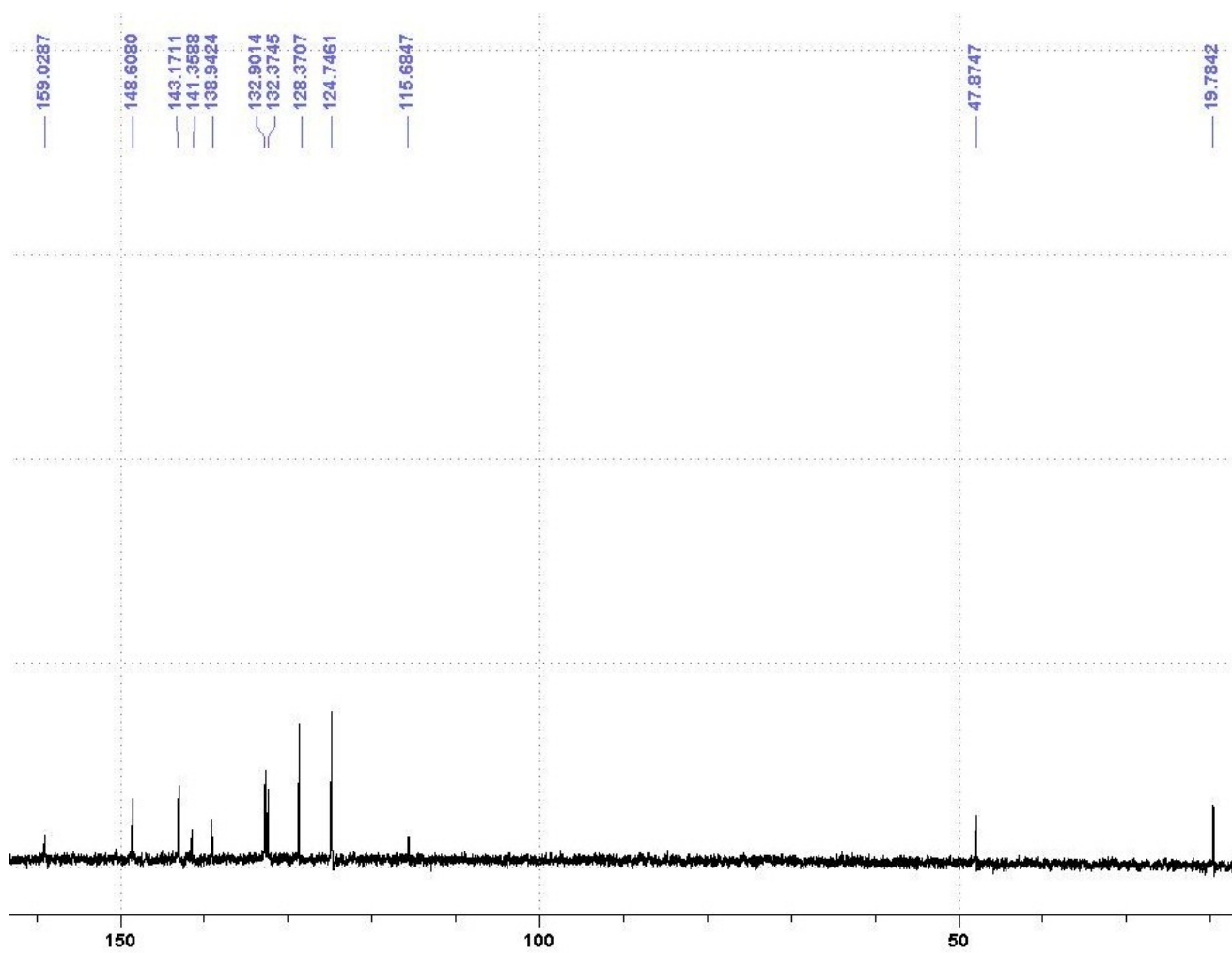


Figure S5. ^{13}C NMR spectrum of *TMPyPZn* in D_2O (rt, 400.13 MHz)

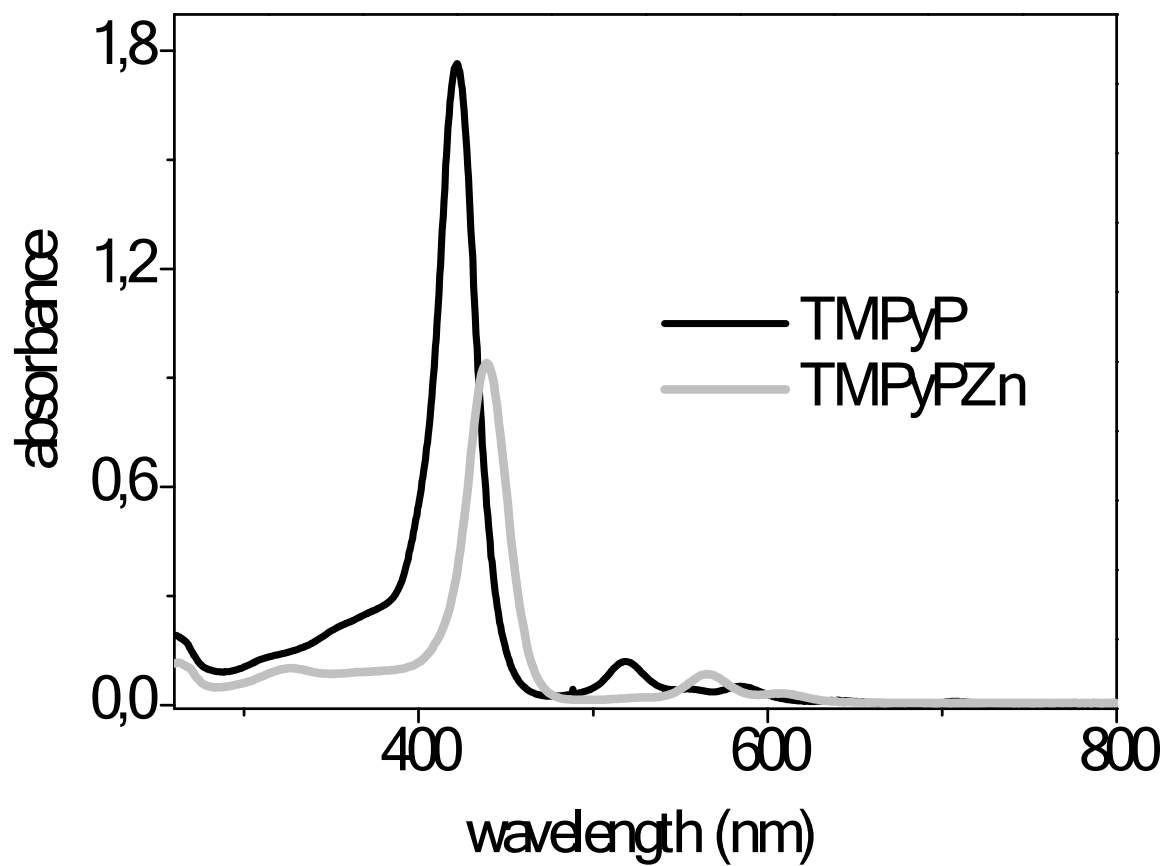


Figure S6. Electronic absorption spectra of TMPyP and *TMPyPZn* (rt, hepes 25 mM, pH 7.4). [TMPyP] = 5 μ M [TMPyPZn] = 5 μ M.

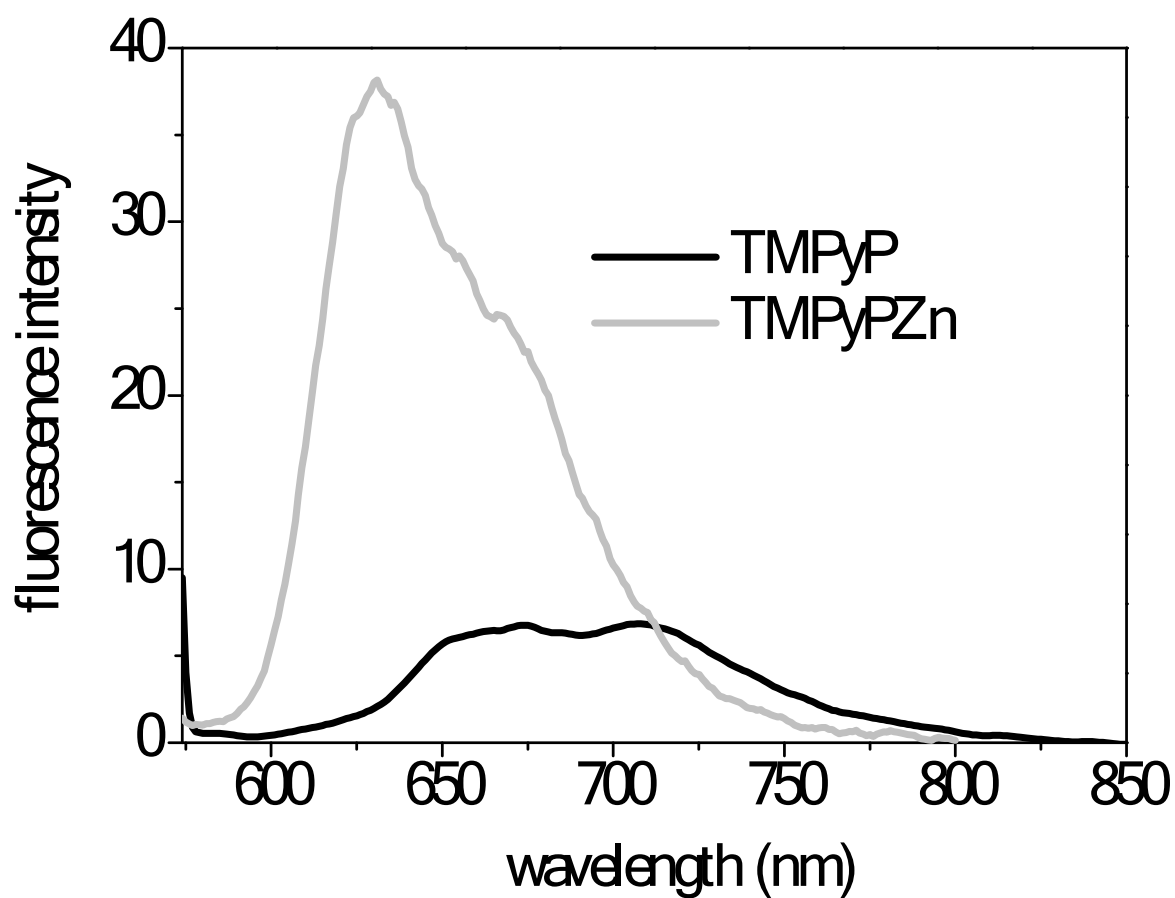


Figure S7. Fluorescence spectra of *TMPyP* and *TMPyPZn* (rt, hepes buffer 25mM, pH 7.4) upon excitation at 563 nm. [TMPyP] = 5 μ M [TMPyPZn] = 5 μ M.

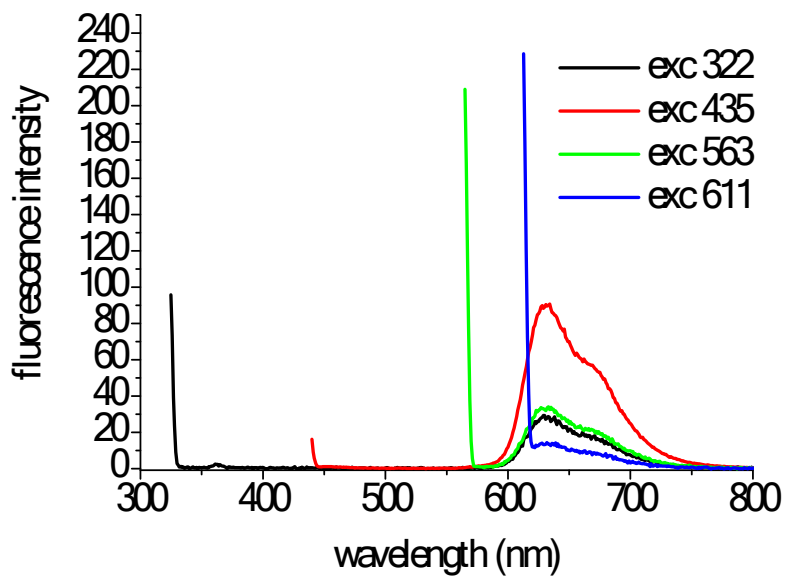


Figure S8. Fluorescence spectra of *TMPyPZn* (rt, hepes buffer 25 mM, pH 7.4) upon excitation at 322, 435, 563 and 611 nm. [TMPyPZn] = 5 μ M.

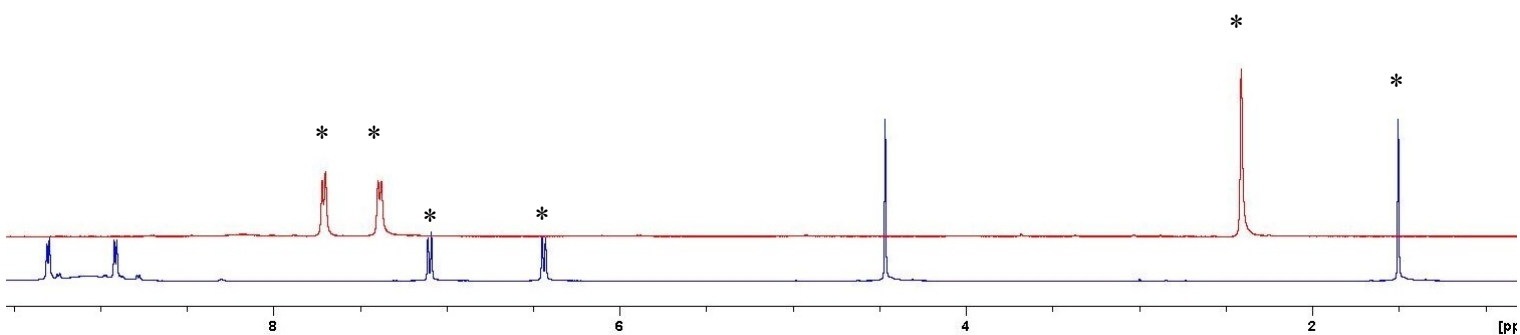


Figure S9. ¹H NMR spectrum of *TMPyP* in D₂O (lower trace), after addition of an excess of HS⁻ (upper trace). Peaks denoted with a (*) correspond to the toluenesulfonate counterion.

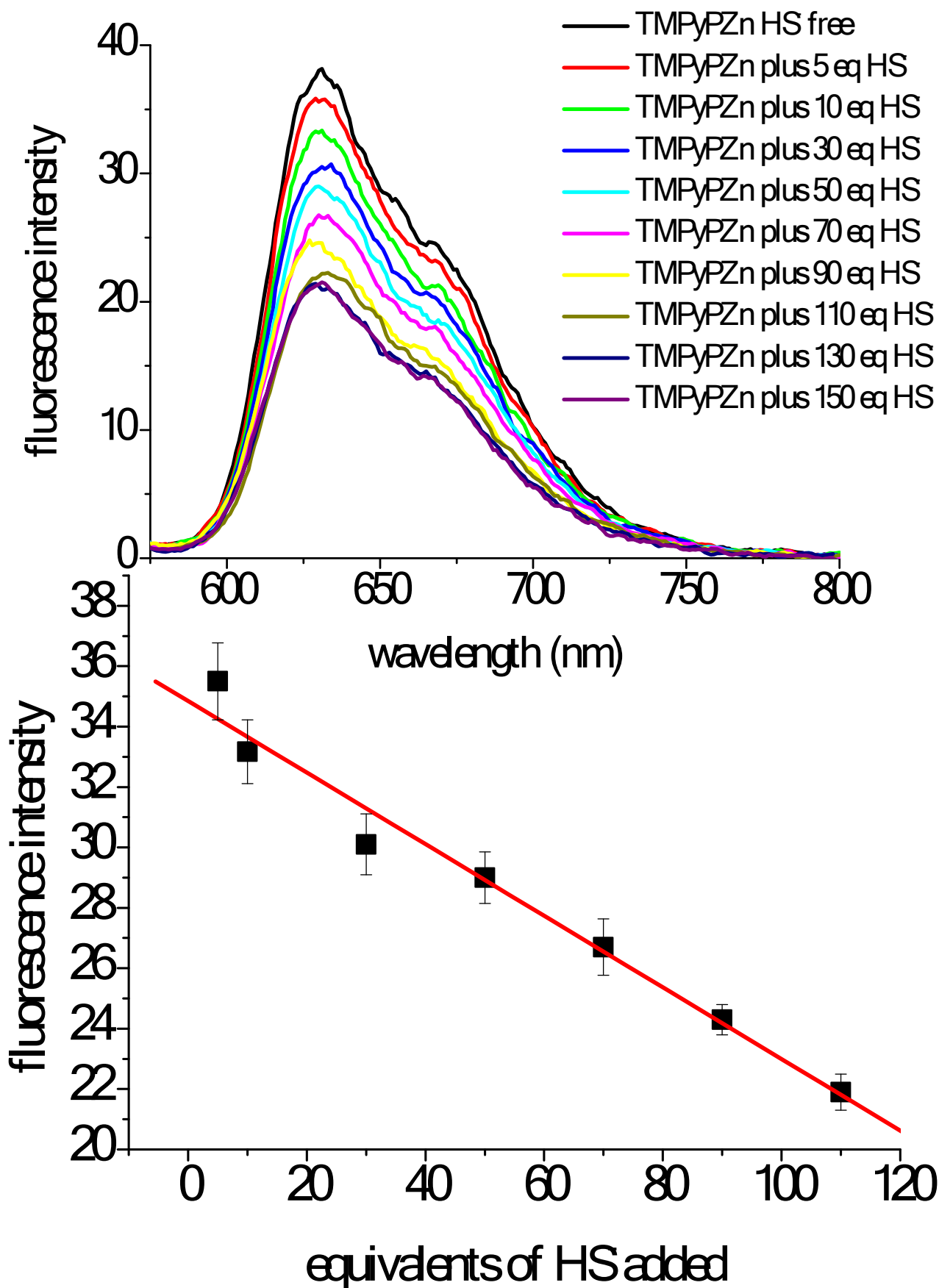


Figure S10. (A) Emission spectra of TMPyPZn (exc 563 nm) when titrated with NaSH (rt, hepes buffer 25 mM, pH = 7.4). [TMPyZn] = $5 \cdot 10^{-6}$ M; end concentration of NaSH varied in the range 25-750 μ M. (B) Fluorescence intensity of the system versus HS⁻ concentration.

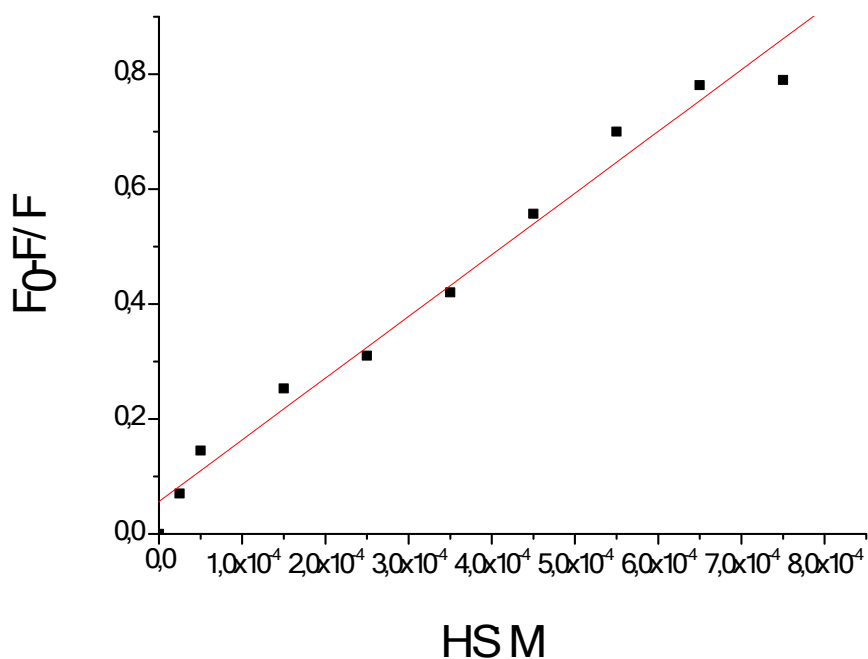
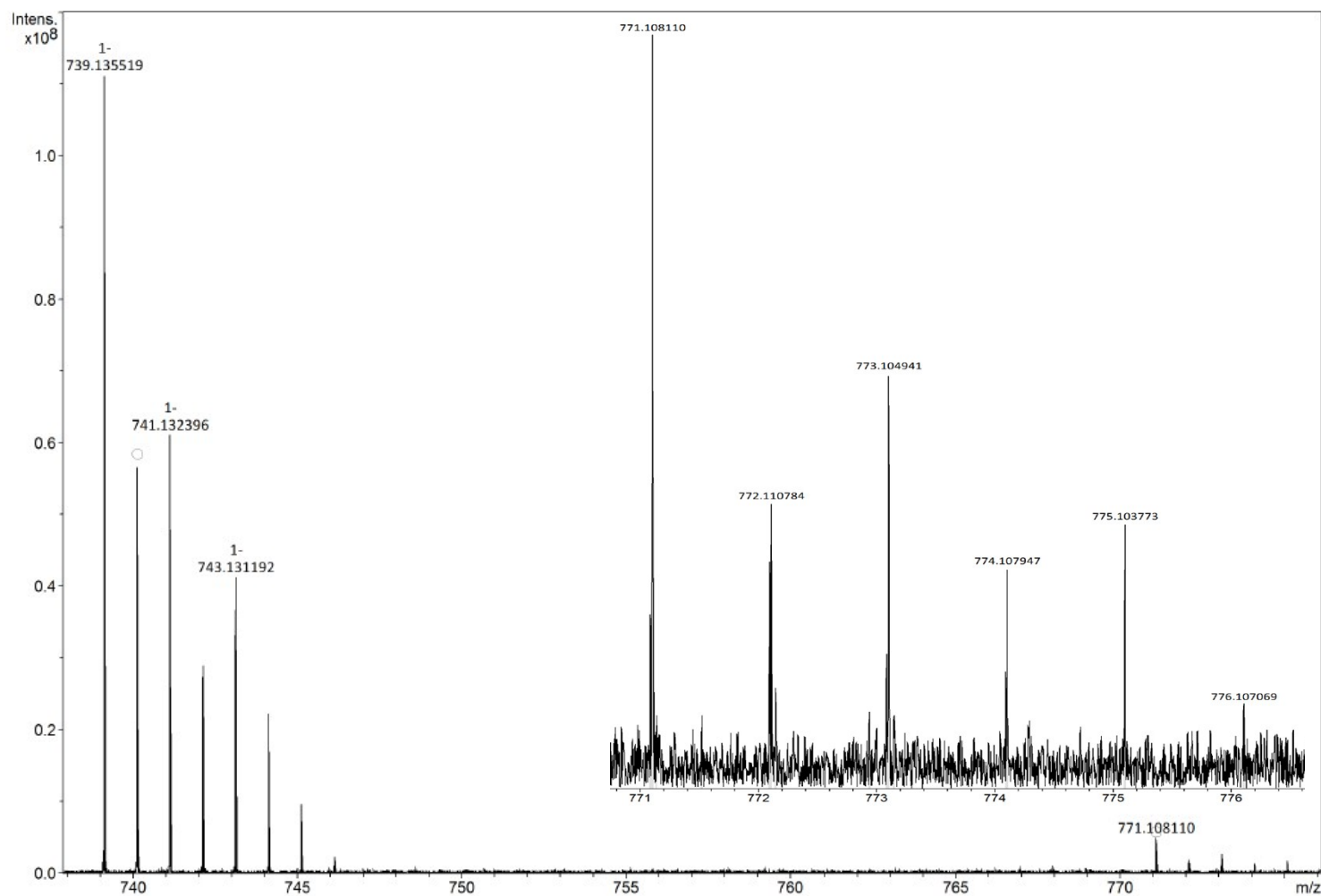


Figure S11. Fluorescence titration of TMPyPZn ($\lambda_{\text{ex}} = 563 \text{ nm}$; $\lambda_{\text{em}} = 630 \text{ nm}$) with NaSH (rt, hepes buffer 25 mM, pH = 7.4). [TMPyZn] = $5 \cdot 10^{-6} \text{ M}$; end concentration of NaSH varied in the range 25-750 μM . F_0 is the fluorescence intensity of the solution without HS^- . The ratio F_0-F/F is plotted versus the total HS^- concentration. The solid line represents the best fit to a linear fitting with a K_b of $1036 \pm 53 \text{ M}^{-1}$. The equation used for data fitting is :¹

$$F_0-F/F = K_b [\text{HS}^-]$$

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Figure S12. HR MALDI-FT-ICR spectrum of the *TMPyPZn-HS* adduct in water solution (ionizing the sample in the negative ion mode) with the enlargement of the zone in the range 771 – 776 m/z.

Reference List

- (1) Lakovicz J.R. *Principles of Fluorescence Spectroscopy*; Kluwer Academic/Plenum, New York, Boston, Dordrecht, Moscow: 1996.