

Highly efficient coordination of Hg^{2+} and Pb^{2+} metals in water with squaramide-coated Fe_3O_4 nanoparticles

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Supporting Information

Table of contents	Page
1. Characterization	1
2. Removal Procedures	8
3. NMR Titrations	9
4. X-Ray Cristal Structure	11

1. Characterization

1.1 Uncoated Fe_3O_4 nanoparticles characterization:

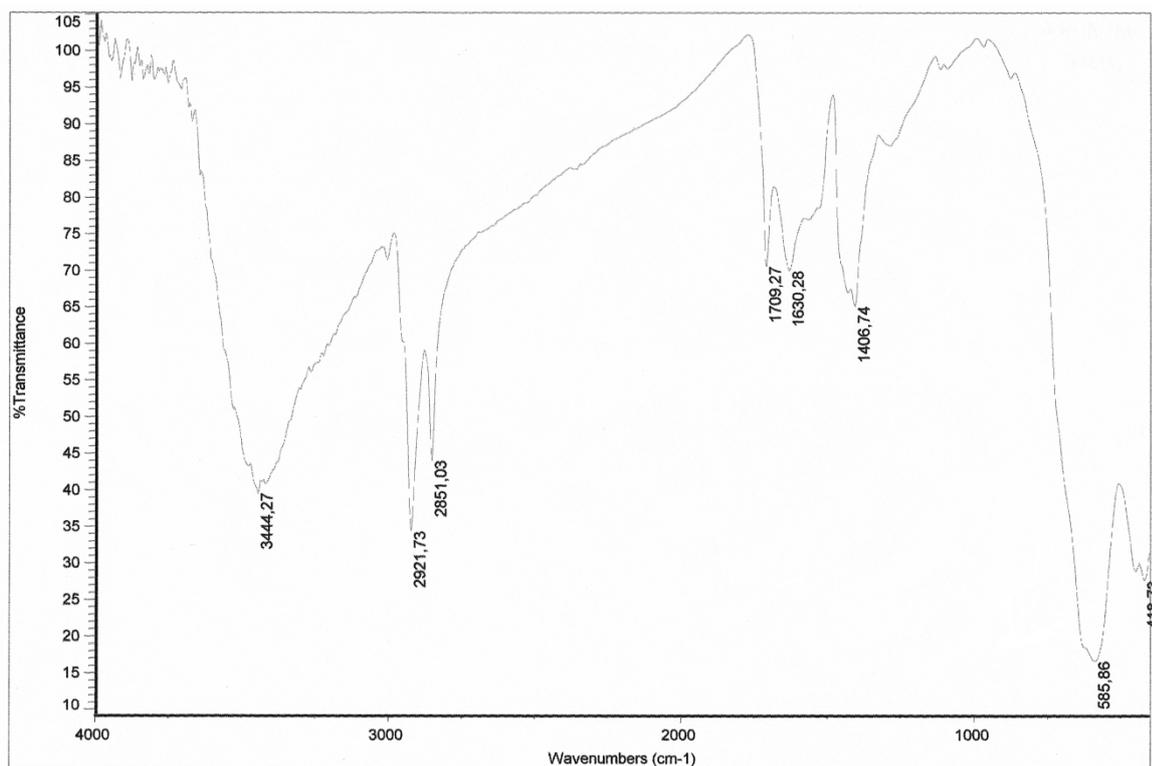
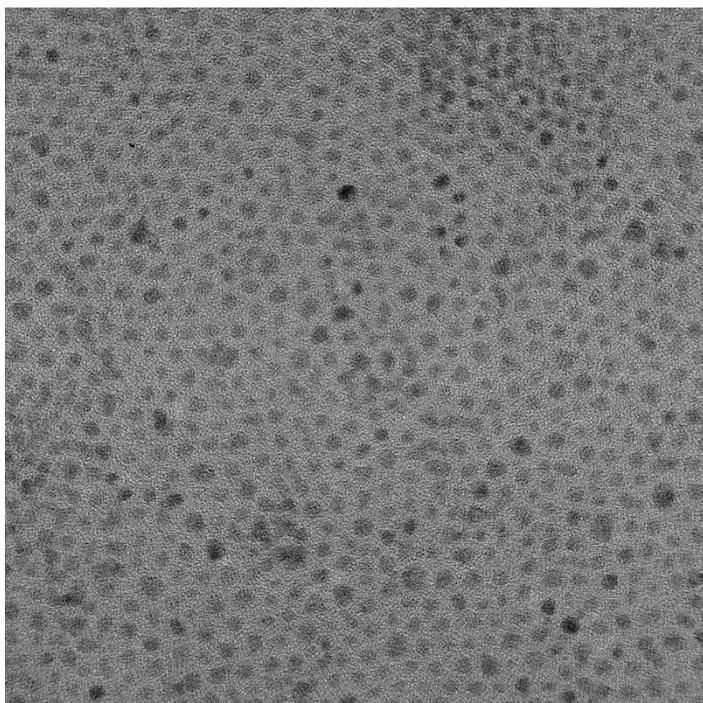


Figure S1. FTIR of Fe_3O_4 nanoparticles.



50 nm

Figure S2. TEM micrograph of Fe₃O₄ nanoparticles.

1.2 Squaramide compounds characterization:

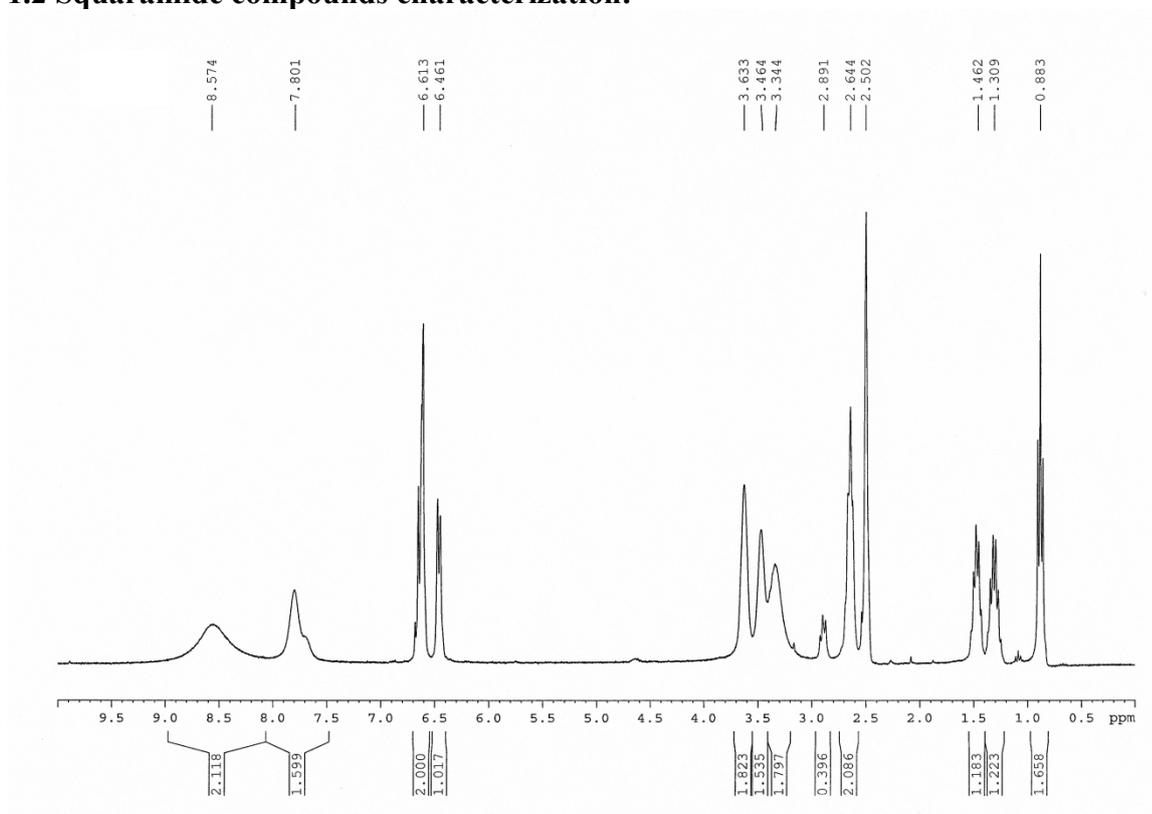


Figure S3. ¹H NMR of squaramide SQ1.

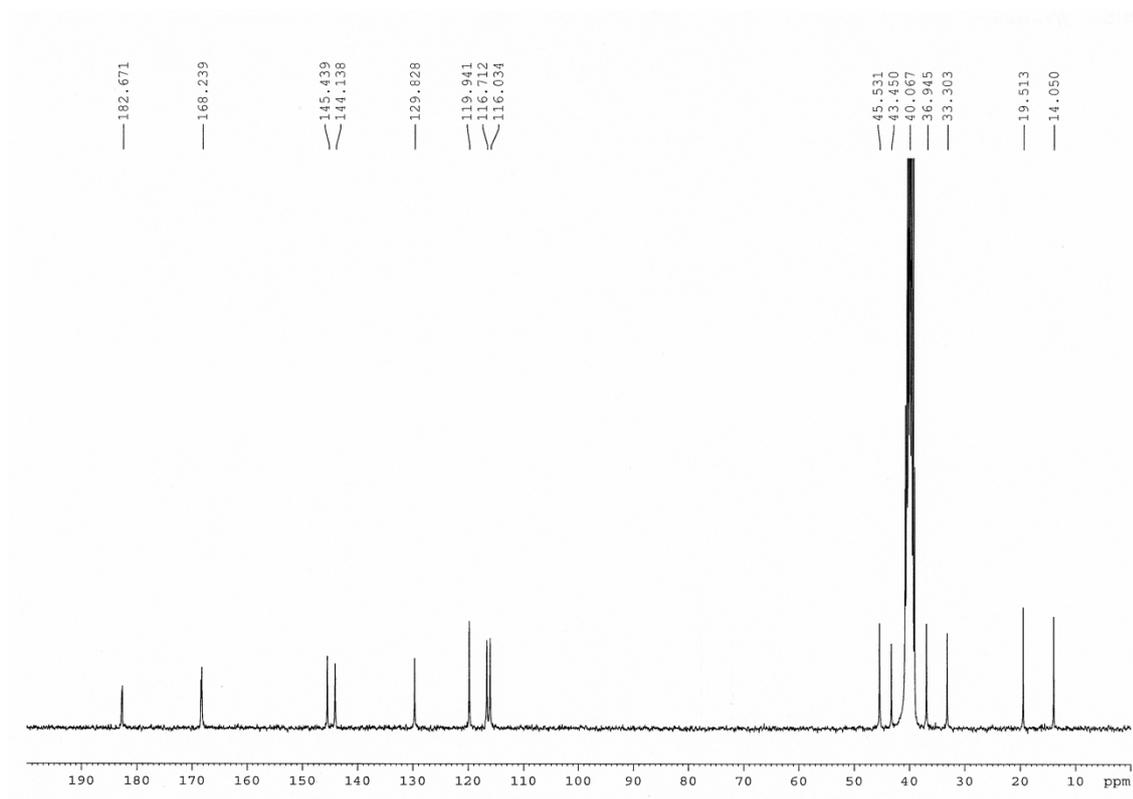


Figure S4. ^{13}C NMR of squaramide SQ1.

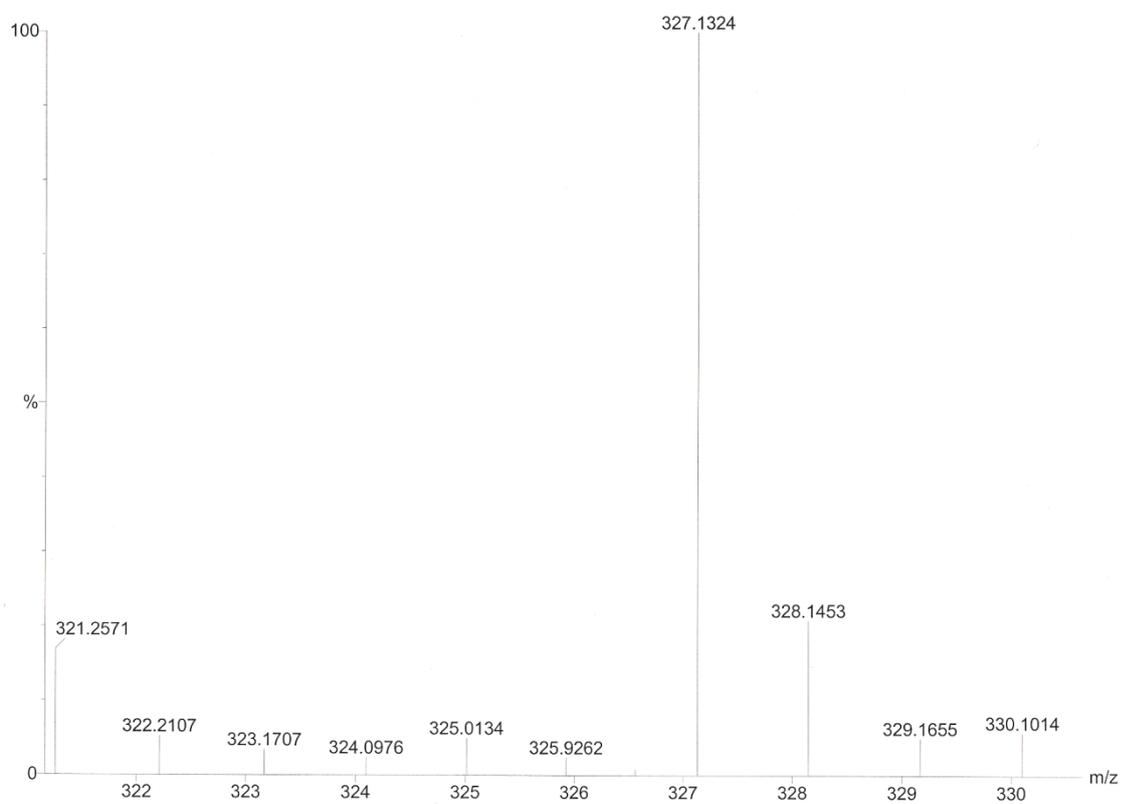


Figure S5. HRMS-ESI(+) of squaramide **SQ1**.

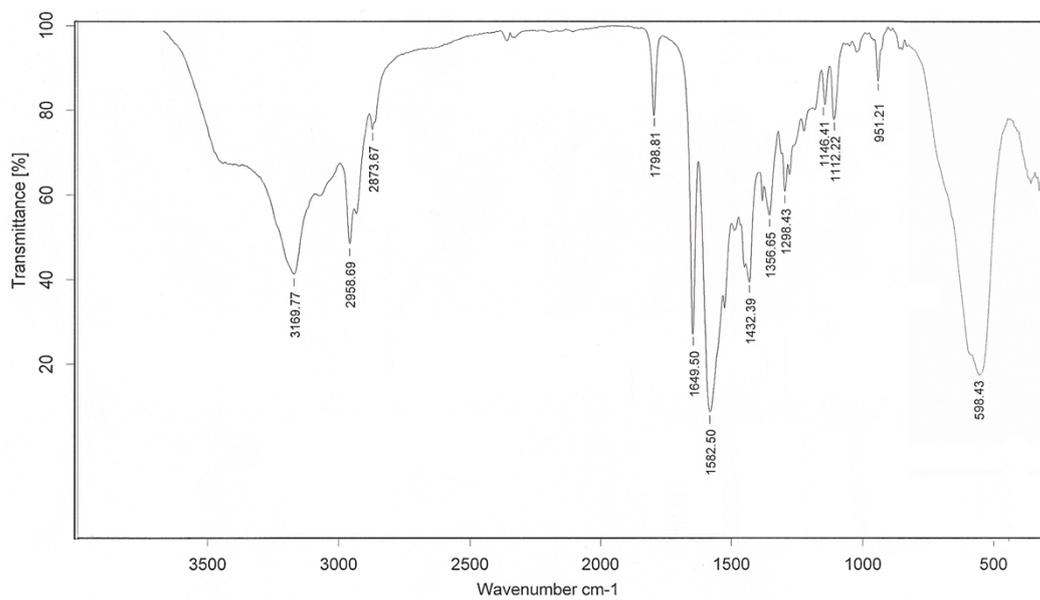


Figure S6. FTIR of squaramide **SQ1**.

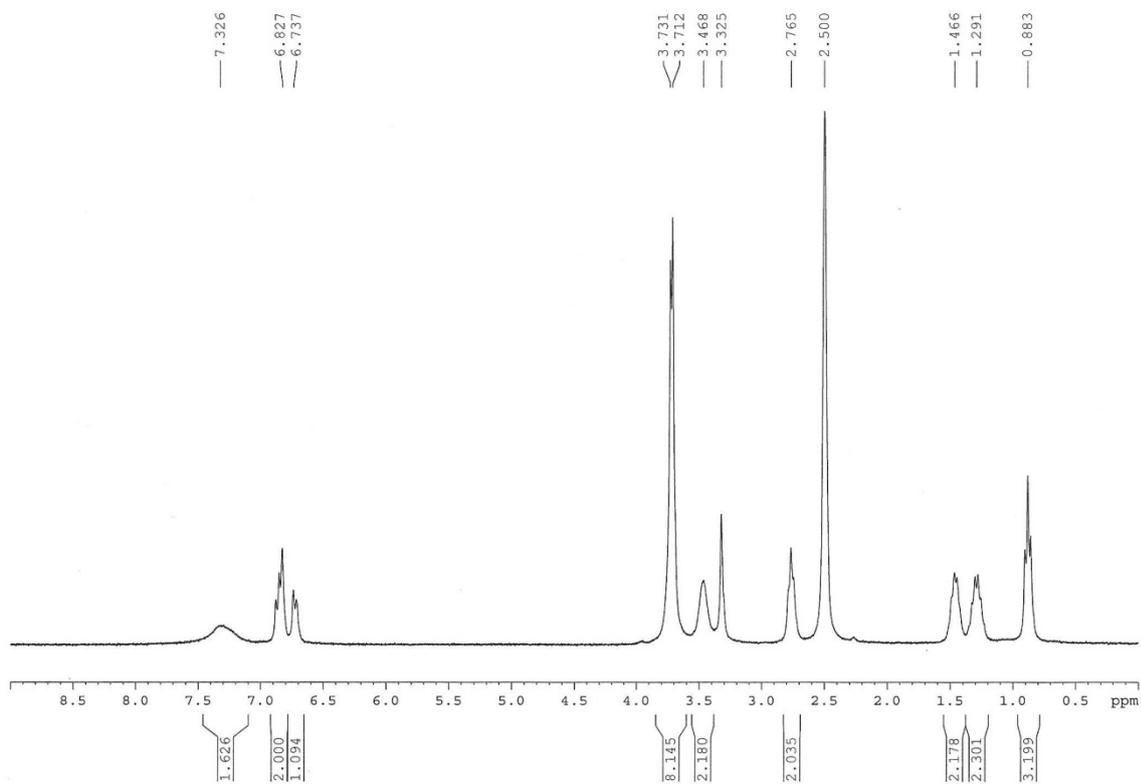


Figure S7. ¹H NMR of squaramide **SQ4**.

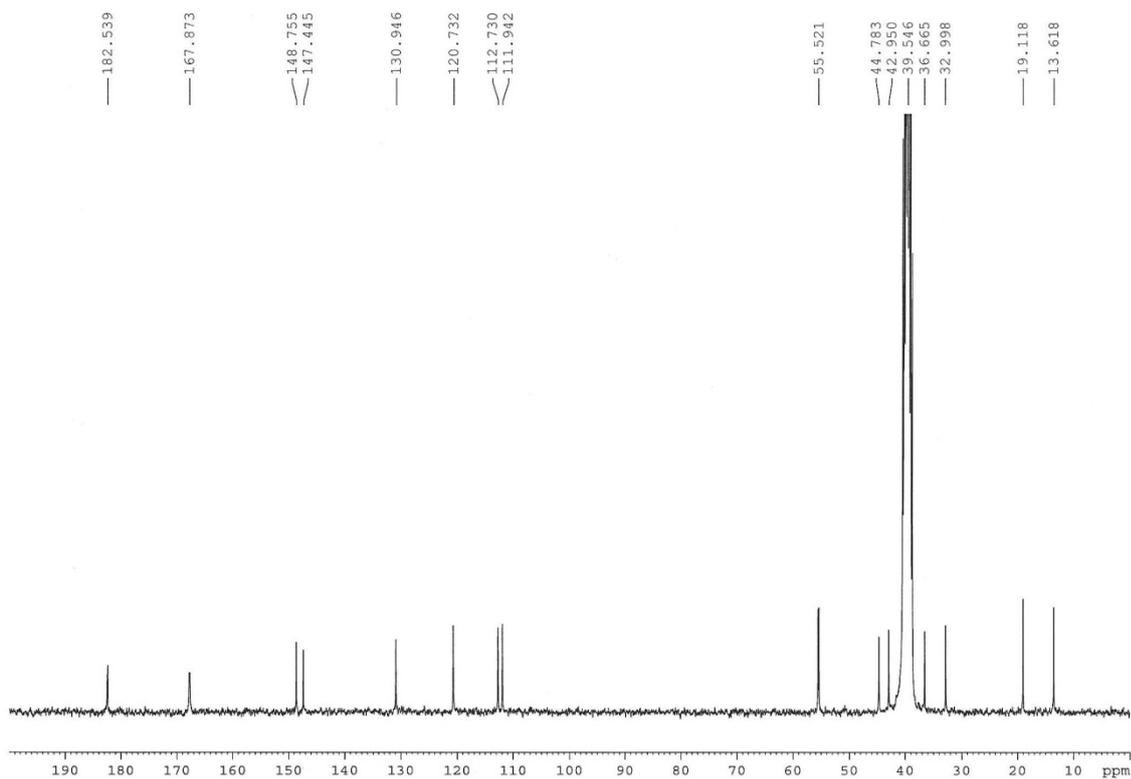


Figure S8. ^{13}C NMR of squaramide **SQ4**.

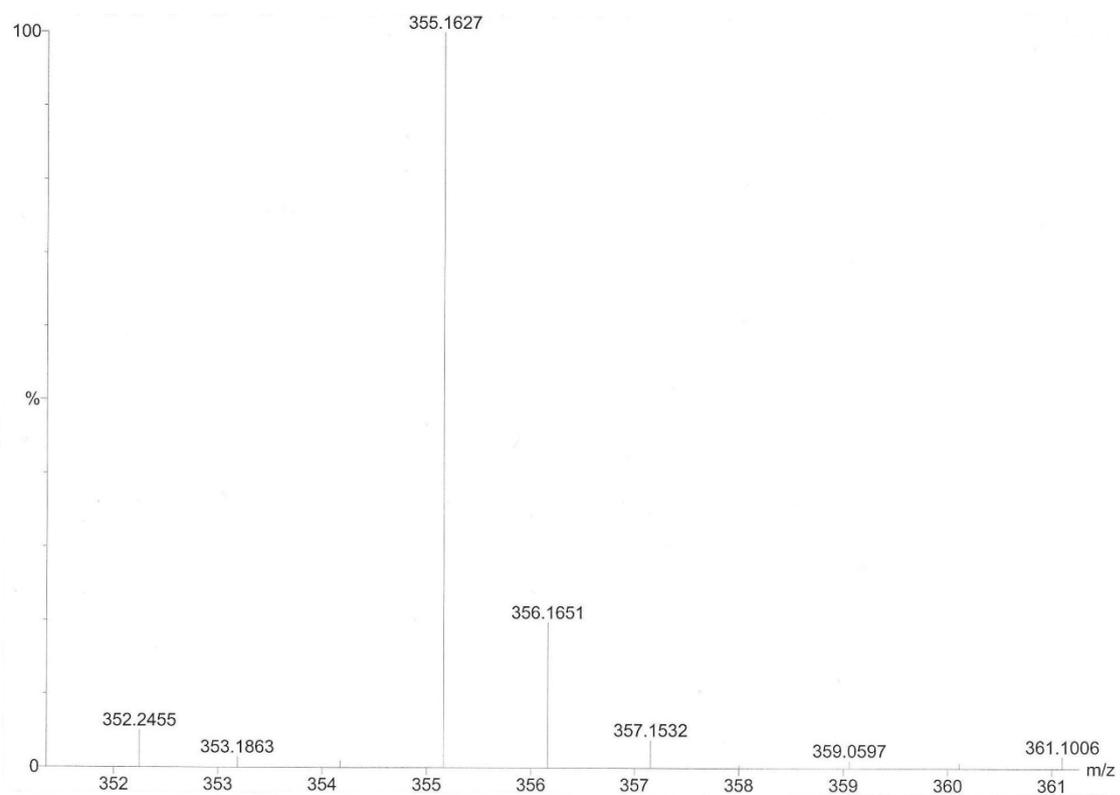


Figure S9. HRMS-ESI(+) of squaramide **SQ4**.

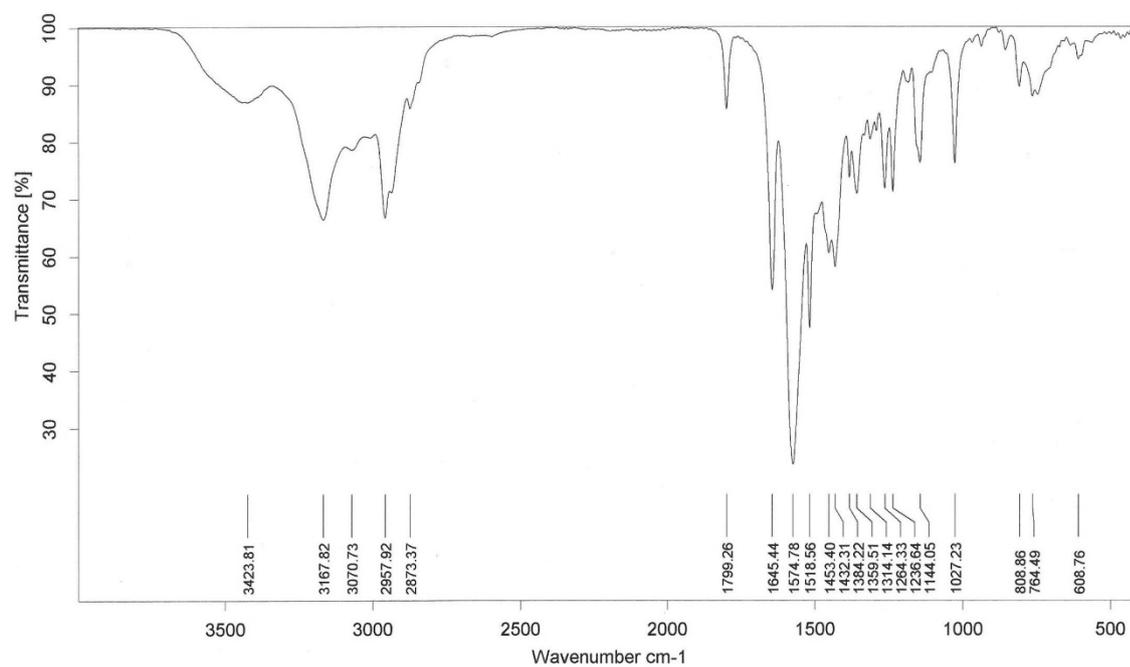


Figure S10. FTIR of squaramide SQ4.

1.3 Estimation of number of residues on NP-SQ1:

The estimation of the number of SQ1 residues on the surface of the nanoparticles was carried out using TEM, ICP and Elemental Analysis.

Through the TEM we determined that the diameter of the Fe₃O₄ nanoparticles was 8 nm. Equations 1 and 2 were used to calculate the number of nanoparticles / mol Fe₃O₄.

$$N = \left(\frac{\pi}{6}\right) \frac{(D)^3 \rho}{MW} \quad (Eq. 1)$$

$$\frac{1}{N} = \frac{\text{nanoparticles}}{\text{mol Fe}_3\text{O}_4} \quad (Eq. 2)$$

Where D is the diameter of the nanoparticles expressed in cm, ρ is the density of Fe₃O₄ (5,196 g/cm³) and MW is the molecular weight of Fe₃O₄ (232,5 g/mol).

For a diameter of 8 nm we obtained 1.67×10^{20} nanoparticles/mol Fe₃O₄.

The elemental analysis of the sample NP-SQ1 determined that the % N content was 1.28%. This value was used to calculate the number of SQ1 molecules / g sample. The result obtained for SQ1 was 2.75×10^{20} molecules/g sample.

Finally, with the ICP analysis we determined that the content of Fe in the sample NP-SQ1 was 0.5 mg Fe/ mg sample. This value was used to determine the mol Fe₃O₄ / g sample (0.00298 mol Fe₃O₄/g sample).

With these three values the number of SQ1 residues was estimated to be 550/nanoparticle.

$$\frac{2.75 \times 10^{20} \text{ SQ1 molec.}}{\text{g sample}} \times \frac{1 \text{ g sample}}{0.00298 \text{ mol Fe}_3\text{O}_4} \times \frac{1 \text{ mol Fe}_3\text{O}_4}{1.67 \times 10^{20} \text{ nanopart.}} = \frac{552 \text{ SQ1 molec.}}{\text{nanopart.}}$$

2. Removal Procedures

2.1 Hg(II) removal with NP-SQ1, NP-SQ2 and NP-SQ3 at different pHs

5 mg of the functionalized nanoparticles NP-SQ1, NP-SQ2 and NP-SQ3 were respectively suspended in 10 mL of Hg(II) solution (5 ppm) in a 15 mL falcon tube. The suspension was irradiated by ultrasound for one minute. The mixture was stirred for 30 minutes. After this period of time, the nanoparticles were isolated by magnetic filtration. The remaining solutions were filtered with 0.45 μm Teflon filter. Finally 5 mL of these solutions were mixed with 1 mL of $\text{K}_2\text{Cr}_2\text{O}_7$ solution (0.5%) and diluted with HNO_3 2.5% to a total volume of 10 mL to analyze by flow injection-hydride generation the Hg(II) concentration remaining.

2.2 Removal procedure for each metal

In a typical removal procedure 5 mg of the functionalized nanoparticles NP-SQ1 were suspended in 10 mL of a metal solution (5 ppm) in a 15 mL falcon tube. The suspension was irradiated by ultrasound for one minute. The mixture was stirred for 30 minutes. After this period of time, the nanoparticles were isolated by magnetic filtration. The remaining solution was filtered with 0.45 μm Teflon filter and finally 2 mL of this solution was diluted with HNO_3 2.5% to a total volume of 10 mL to analyze by ICP the metal concentration remaining.

2.2.1 Calculated solid phase partition coefficient K_d

$$K_d = \frac{C_0 - C_f}{C_f} \times \frac{V}{M} \quad (\text{Eq. 3})$$

Where C_0 and C_f are the initial and final concentrations of the metal in solution, V is the volume of the solution in mL, and M is the mass of the NP-SQ1 in g.

2.3 Removal procedure using a solution containing each metal

5 mg of the functionalized nanoparticles NP-SQ1 were suspended in 10 mL of the metals solution (5 ppm of Cd(II), Pb(II), Hg(II), Zn(II), Cu(II), Co (II) and Cr(III)) in a 15 mL falcon tube. The suspension was irradiated by ultrasound for one minute. The mixture was stirred for 30 minutes. After this period of time, the nanoparticles were isolated by magnetic filtration. The remaining solution was filtered with 0.45 μm Teflon filter and finally 2 mL of this solution was diluted with HNO_3 2.5% to a total volume of 10 mL to analyze by ICP the metals concentration remaining.

3. NMR Titrations

Titration were carried out at room temperature in CD₃CN solvent. Host concentration (5x10⁻³M) was kept constant. 25 additions of increasing volumes of a Guest solution (0.075M) were added and the NMR spectrum was registered.

For Pb²⁺ titration the whole set of NMR data, corresponding to NH, ArH, and aliphatic protons were fit using HypNMR10 (Protonic Software, version 2008) according to the model in table S1, where β is defined by Eq. 4 and 5.

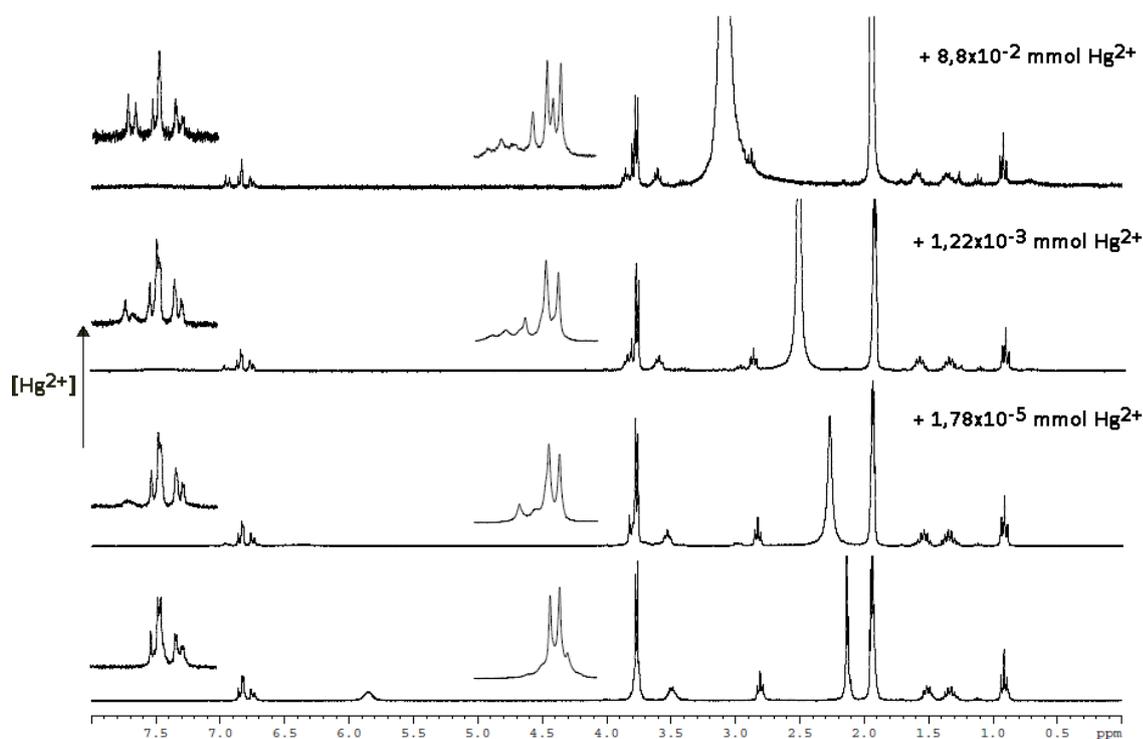


Figure S11. Summary of ¹H NMR titration of SQ4 and Hg²⁺ in CD₃CN. An extension of the 3.7 – 3.9 and the 6.6 - 7.0 zone is presented.

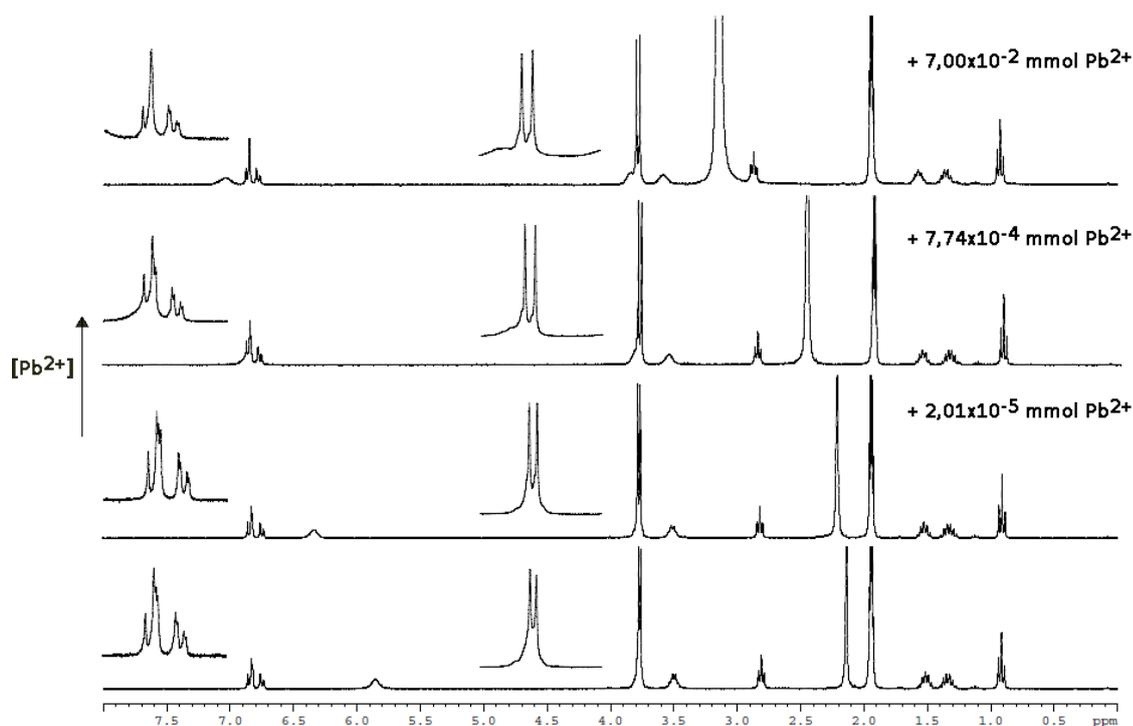


Figure S12. Summary of ^1H NMR titration of SQ4 and Pb^{2+} in CD_3CN . An extension of the 3.7 – 3.9 and the 6.6 - 7.0 zone is presented.

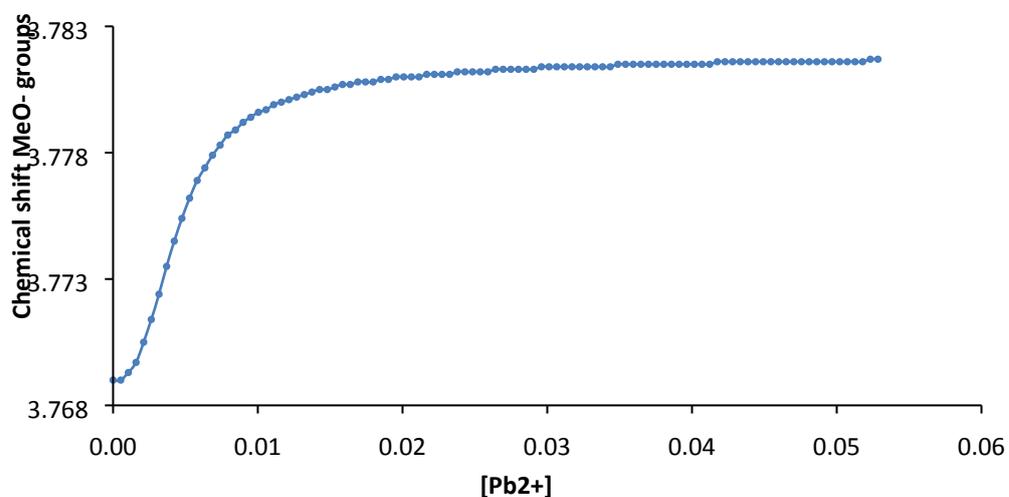


Figure S13. Fitting of the ^1H NMR titration data in CD_3CN at 298K of SQ4 and Pb(II). Data points represent the experimental chemical shifts (δ) of methoxy protons. Lines are best-fit curves calculated by nonlinear regression.

Table S1. Data obtained from titration between SQ4 and Pb(II).

Complexation	Log β	H	G	
$\text{H} + \text{G} \rightleftharpoons \text{HG}$	3.50 ± 0.06	1	1	refined
$2\text{H} + \text{G} \rightleftharpoons \text{H}_2\text{G}$	5.80 ± 0.06	2	1	refined

4. X-Ray Cristal Structure

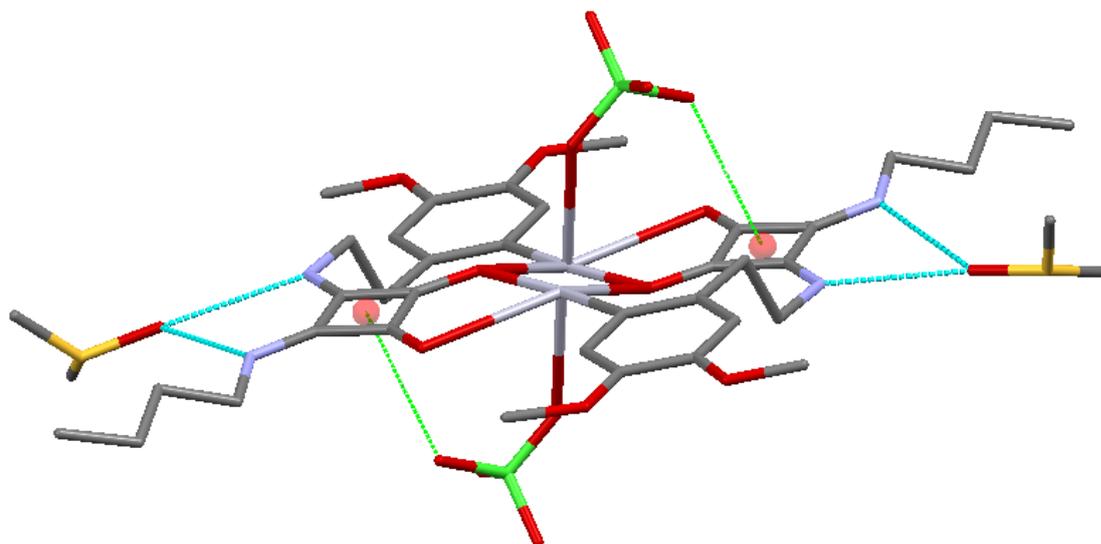


Figure S14. Anion- π and H-bond interactions in the complex unit.