Supporting Information

Novel Material for the Detection and Removal of Mercury (II) Based on 2,6-bis(2-thienyl)pyridine Receptor.

Jacquelyn G. Egan, Andrew J. Hynes, Holly M. Fruehwald, Iraklii I. Ebralidze, Sarah D. King, Reza Alipour Moghadam Esfahani, Fedor Y. Naumkin, E. Bradley Easton, Olena V. Zenkina*

Faculty of Science, University of Ontario Institute of Technology, 2000 Simcoe Street North, Oshawa, ON L1H 7K4, Canada.

Content

Figure S1. Jobs plot for formation of L-Hg^{2+}
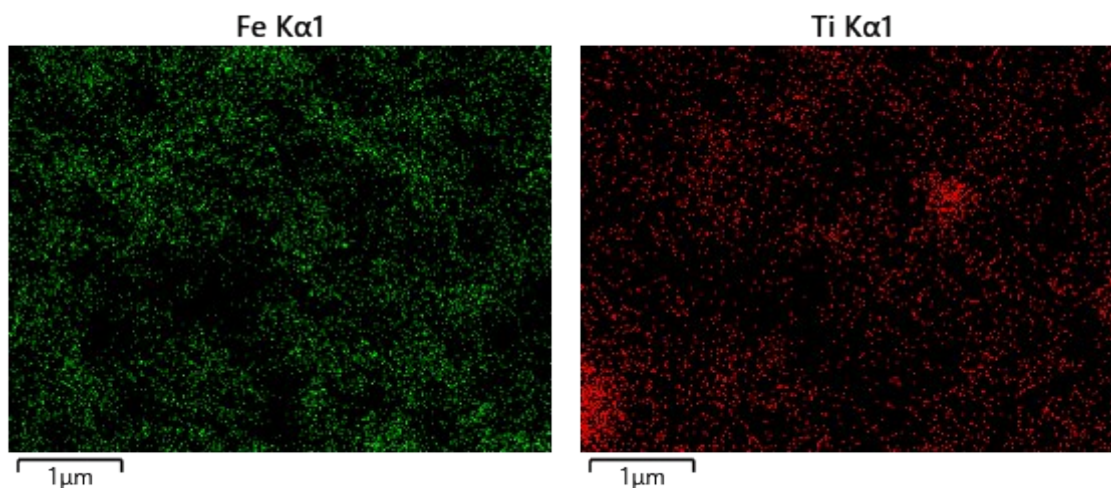
Figure S2. Energy-dispersive X-ray spectroscopy (EDX) mapping of Fe$_3$O$_4$@TiO$_2$ NP
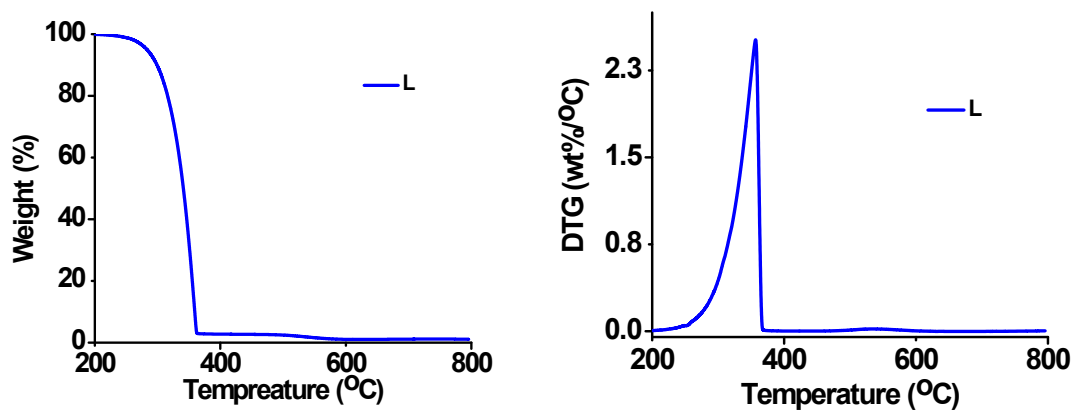
Figure S3. A) Thermogavimetric analysis (TGA) of L under argon and B) Differential Thermal Analysis (DTA) of L under argon.
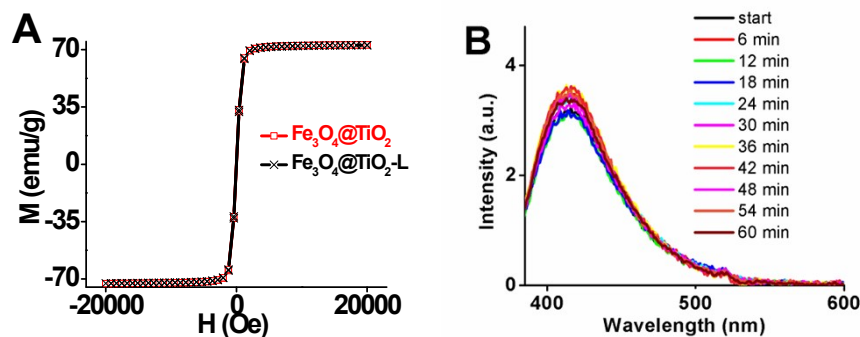
Figure S4. A: Magnetic hysteresis curves of $Fe_3O_4@TiO_2$ and $Fe_3O_4@TiO_2$-L nanomaterials at 300K. **B:** Fluorescence measurements (excitation wavelength 330nm) of $Fe_3O_4@TiO_2$-L (1.0 mg) in anhydrous acetonitrile (3.0 mL) taken every 6 minutes in sealed 1 x 1 cm cuvette.
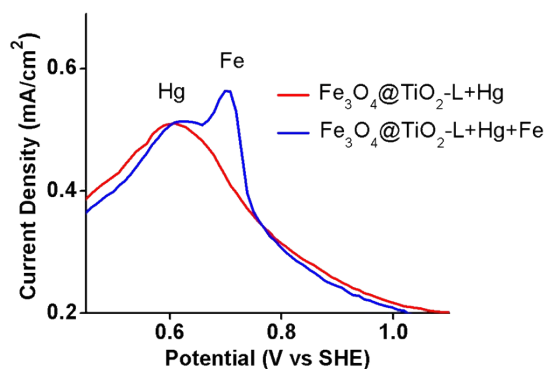
Figure S5. Differential pulse voltammetry (DPV) response of the $Fe_3O_4@TiO_2$-L deposited on glassy carbon electrode and stepwise exposed to Hg^{2+} and Fe^{3+} in 0.1M H_2SO_4.

Synthesis of the ligand 2,6-di(thiophen-2-yl)-4,4'-bipyridine (L)
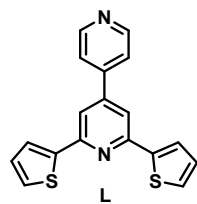
Ligand L was synthesized according to previously published procedure.[1, 2]

L: ^{1}H-NMR (400 MHz, DMSO-d$_6$) δ 8.79 (dd, J = 4.4, 1.7 Hz, 2H), 8.21 (s, 2H), 8.07 (dd, J = 3.7, 1.1 Hz, 2H), 8.04 (dd, J = 4.5, 1.7 Hz, 2H), 7.71 (dd, J = 5.0, 1.1 Hz, 2H), 7.23 (dd, J = 5.0, 3.7 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 152.99 (s), 150.91 (s), 147.12 (s), 144.68 (s), 144.31 (s), 129.58 (s), 128.94 (s), 126.85 (s), 114.85 (s), FT-IR: ν/cm^{-1} 3044w (C-H aromatic), 2100w (C-H aromatic), 1535m (C=S), 1455s (C=C-C), 1066m (C-H aromatic), 817vs (C-H aromatic), 691vs (C-H aromatic). ESI-MS: For $C_{18}H_{12}N_2S_2$ predicted 320.44, found (M+1) 321.05.

Synthesis of the 1-methyl-2',6'-di(thiophen-2-yl)-[4,4'-bipyridin]-1-ium ligand (QL)
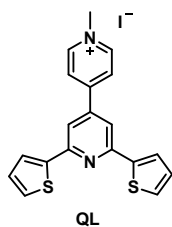
Following a literature procedure,[3] a reflux system was assembled whilst hot and flushed with $N_{2(g)}$. To the round bottom flask **L** (0.16 mmol), acetonitrile (25 mL) and methyl iodide (0.78 mmol) were added then heated to 40°C whilst stirring. Upon reaching 40°C the reaction mixture was refluxed for 24 hours. Once cooled to room temperature, the solvent was removed by a rotary evaporator and the powder dried *in vacuo* to give 1-methyl-2',6'-di(thiophen-2-yl)-[4,4'-bipyridin]-1-ium as a bright yellow solid, **QL** (35 mg, 67%).

QL ^{1}H-NMR (400 MHz, DMSO-d_6) δ 9.19 (d, J=6.8 Hz, 2H), 8.81 (d, J=6.8Hz, 2H), 8.40 (s, 2H), 8.09 (dd, J=3.7, 1.0 Hz, 2H), 7.74 (dd, J=5.0, 1.0 Hz, 2H), 7.25 (dd, J=5.0, 3.7 Hz, 2H) 4.39 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.65 (m), 146.94 (s), 141.4 (s), 138.73 (s), 138.27 (s), 125.08 (s), 123.94 (s), 122.29 (s), 120.45 (s), 110.15 (s), 42.93 (s) FT-IR: v/cm[-1] 2991w (C-H aromatic), 2100w (C-H aromatic), 1539m (C=S), 1419s (C=C-C), 830s (C-H aromatic), 709vs (C-H aromatic).

Synthesis of L-Hg^{2+} metal complex
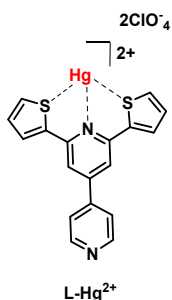
Corresponding mercury complex **L-Hg^{2+}** was formed when a solution of 30.2 mg (0.076 mmol) of mercury(II) perchlorate hydrate in acetonitrile (2 mL) was added to a solution of **L** (24.2 mg, 0.076 mmol) in acetonitrile (3 mL). After 30 min yellow precipitate was filtered out and washed with 50 mL of hexanes resulting in 10 mg, 25.4% yield of complex **L-Hg^{2+}**.

For **L-Hg^{2+}** ^{1}H NMR: (400.00 MHz, CD$_3$CN): δ 8.88 (d, $^3J_{HH}$ = 6.1 Hz, 1H), 8.49 (d, $^3J_{HH}$ = 6.2 Hz, 1H), 8.07 (s, 1H), 7.92 (d, $^3J_{HH}$ = 3.6 Hz, 1H), 7.65 (d, $^3J_{HH}$ = 5.0 Hz, 1H), 7.26 (m, 1H).^{13}C NMR (101 MHz, CD$_3$CN): δ 155.99 (C_q), 153.12 (C_q), 142.53, 130.47, 129.13, 127.70, 126.26, 126.22(C_q), 116.5. Assignments for quaternary carbons were made by comparison of ^{13}C NMR to DEPT 135-NMR. ESI-MS: For C$_{18}$H$_{12}$ HgN$_2$S$_2$$^{2+}$ predicted 261.00, found (M-1) 260.11, (M-3) 258.04, (M-3+K) 283.05.

Synthesis of QL-Hg^{2+} metal complex

The **QL-Hg^{2+}** complex was synthesized by addition to the solution of of mercury(II) perchlorate hydrate (23.4 mg, 0.058 mmol) in acetonitrile (2 mL) to a solution of **L** (27.0 mg, 0.058 mmol) in acetonitrile (3 mL) After 30 min, the yellow precipitate was filtered out and washed with 50 mL of hexanes resulting in 7.6 mg, 17.8% yield of complex **QL-Hg^{2+}**. ^{1}H NMR (400 MHz, CD$_3$CN) δ 8.81 Hz (d, $^3J_{HH}$ = 7.24 Hz, 1H) 8.46 Hz (d, $^3J_{HH}$ = 7.24 Hz, 1H) 8.09 Hz (s, 1H) 7.94 Hz (d, $^3J_{HH}$ = 4.84 Hz, 1H) 7.71 Hz (d, $^3J_{HH}$= 6.04 Hz, 1H) 7.28 Hz (m, 1H) 4.39 (s, 3H). ^{13}C-NMR (101 MHz, CD$_3$CN) δ: 153.1(C_q), 152.6(C_q), 145.9, 144.7(C_q), 137.7(C_q), 130.2, 128.7, 127.7, 126.1, 116.1, 48.21

Synthesis of the Fe₃O₄ NP

The synthesis was carried out according to a previously reported method with modification,[4, 5] 2.5g of FeCl₃•6H₂O was allowed to stir in 75 mL of ethylene glycol until it dissolved. Then 7.2g of sodium acetate and 2g of polyethylene glycol (PEG) 4000 were added to the above solution and stirred until all the reactants dissolved. The mixture was then transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated to and maintained at 160°C for 8 hours and then naturally cooled to room temperature. The product mixture was centrifuged, the liquid was discarded while the solids were washed with ethanol and water. The magnetite product was dried under vacuum at 90°C for 10 hours.

Synthesis of the Fe₃O₄@TiO₂ NP

Based on a pervious method,[6] 100 mg of Fe₃O₄ microspheres were dispersed in 100 mL of an ethanol/ acetonitrile (3/1, v/v), followed by the addition of 1 mL concentrated (28%) ammonia solution under sonication for 20 minutes. Afterwards 1.6 mL of tetrabutyl titanate (TBOT) in 30 mL of ethanol/ acetonitrile (3/1, v/v) was added dropwise under continuous sonication. The mixture was then allowed to stir under sonication for 2 hours then transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated to and maintained at 160°C for 24 hours and then naturally cooled to room temperature. The product mixture was centrifuged, the liquid was discarded while the solids were washed with ethanol and water. The product was then dried under vacuum at 100°C overnight. The powder was sonicated in solutions of ethanol and water multiple times then separated with a magnet to remove any unreacted TiO₂.

Synthesis of Fe₃O₄@TiO₂-L NP

The solid substrate Fe₃O₄@TiO₂ NP was functionalized by the molecular receptor **L** by two step procedure using chlorobenzylsiloxane-based templating layer according to an adapted literature procedure.[7]

Under N₂ atmosphere, Fe₃O₄@TiO₂ NP substrate was submerged into a solution of trichloro(4-(chloromethyl)phenyl)silane with anhydrous hexane (1:200 v/v) for 20 min. The material was washed 3x with anhydrous hexane then with anhydrous acetonitrile, and sonicated 1x for 5 min per solvent. Then the material was submerged into the solution of **L** (0.2 mM) in anhydrous acetonitrile and sealed in a pressure tube. The material was heated for 96 h at 95°C without light.

After cooling down, the resulting $Fe_3O_4@TiO_2$–L NP material was washed 3x with anhydrous hexane then anhydrous acetonitrile, and sonicated 1x for 5 min per solvent.

Determining selectivity of L to various metal ions in acetonitrile.

A stock solution of **L** was made in acetonitrile to give a final concentration of 9.98×10^{-3} mM. Eight metal (Fe^{2+}, Fe^{3+}, Cr^{3+}, Zn^{2+}, Co^{2+}, Ru^{3+}, Cd^{2+}, Cu^{2+}) solutions were prepared by dissolving the corresponding metal salt in acetonitrile. An aliquot of the L stock solution (9.98×10^{-3} mM) was transferred to a 10 mm x 10 mm quartz cuvette. The fluorescence emission was measured using λ_{ex} = 330 nm and λ_{em} = 340 – 640 nm. An aliquot of the first metal solution was added to the cuvette, stirred for 2 minutes, then the fluorescence emission of M+L was measured. Hg^{2+} was then added to the cuvette, stirred for 2 minutes before the fluorescence emission of M + L + Hg^{2+} was obtained. These steps were repeated for all eight metal salts.

Fluorescence emission experiment of L-Hg^{2+} complex formation

A stock solution of Hg^{2+} was prepared by dissolving $Hg(ClO_4)_2$ in acetonitrile. An aliquot of the **L** stock solution (1×10^{-4} mM) was transferred to a 10 mm x 10 mm quartz cuvette. Additions of Hg^{2+} were added via a microsyringe to the **L** aliquot solution until the fluorescence peak at 413 nm was fully quenched. Between each addition step, the solution was mixed for 30 sec before the fluorescence emission was measured. Experiment was performed two times under excitation wavelengths of 325 and 385 nm, respectively. When the sample was exited under 385 nm upon addition of mercury, in addition to the disappearance of the peak at 413 nm, the growing of the new emission peak at 580 nm was observed. See **Figure 3** in the main manuscript for details.

Determination of fluorescence quantum yields for L and L-Hg^{2+}

a) Quantum Yield of **L** at 413 nm

The fluorescent standard sample to be used is *L*-tryptophan as its λ_{abs} and λ_{em} are similar to that of the **L** test sample. A stock solution of *L*-tryptophan was prepared by dissolving *L*-tryptophan (20 mg) in DI water to give a concentration of 10 mM. This was followed by two further dilutions of the solution to give a final concentration of 0.2 mM. The fluorescence emission was measured using λ_{ex} = 280 nm and λ_{em} = 290 – 500 nm. This was repeated for the L test sample, where the solvent background used was acetonitrile and the concentrations of the five dilutions were 1.11×10^{-3} mM, 2.22×10^{-3} mM, 3.33×10^{-3} mM, 4.44×10^{-3} mM and 5.55×10^{-3} mM. Fluorescence emission was measured using λ_{ex} = 330 nm and λ_{em} = 340 – 550 nm. The integrated fluorescence intensity was plotted against the absorbance at the fluorometer excitation wavelength. This is at 280 nm for *L*-tryptophan and 330 nm for **L**. A linear regression line was fitted to the resulting graph, of which the gradient is required for the quantum yield calculation.

Equation S1[8] is required to calculate the fluorescence quantum yield:

$$\varphi_x = \varphi_{STD}\left(\frac{m_x}{m_{STD}}\right)\left(\frac{\eta_x^2}{\eta_{STD}^2}\right)$$

Eq. S1

Where 'x' denotes the complex (test sample) and 'STD' denotes L-tryptophan (standard sample). φ represents the quantum yield, m represents the gradient of the plot of integrated fluorescence intensity vs absorbance, and η represents the refractive index of the solvent used.

Propagation of error for quantum yield calculations. Equation S2 was used to calculate the standard deviation from quantum yield.

$$\sigma_x = \varphi_x \sqrt{\left(\frac{\sigma_{mx}}{m_x}\right)^2 + \left(\frac{\sigma_{mSTD}}{m_{STD}}\right)^2 + \left(\frac{\sigma_{\varphi STD}}{\varphi_{STD}}\right)^2}$$

Eq.S2

Table S1. Variables for calculation of the standard deviation from quantum yield for **L**

Parameter	Value	Standard Error (±)
Quantum Yield, ϕ_x, L	0.21	0.08
m_x	2.88×10^5	1.07×10^4
m_{STD}	1.59×10^5	2.27×10^4
ϕ_{STD}	0.12	0.01
$\sigma_{mx} = standard\ error\ of\ m_x * \sqrt{N}$	2.14×10^4	-
$\sigma_{mSTD} = standard\ error\ of\ m_{STD} * \sqrt{N}$	4.55×10^4	-

The standard deviation from quantum yield for **L** was calculated using equation 2.

$$\sigma_x = 0.21 \sqrt{\left(\frac{2.14 \times 10^4}{2.88 \times 10^5}\right)^2 + \left(\frac{4.55 \times 10^4}{1.59 \times 10^5}\right)^2 + \left(\frac{0.01}{0.12}\right)^2} = 0.08$$

b) Quantum Yield of **L**–Hg^{2+} Complex at 585 nm

The quantum yield of **L**–Hg^{2+} was determined using the fluorescent standard sample Ru(bipy)$_3$ as its λ_{abs} and λ_{em} are similar to that of the **L**–Hg^{2+} complex test sample.[9] A stock solution of Ru(bipy)$_3$ was prepared by dissolving Ru(bipy)$_3$ (2.5 mg) in DI water (20 mL) to give a concentration of $2.0*10^{-4}$ M. A stock solution of **L**–Hg^{2+} was prepared by dissolving L (42.8 mg) and Hg(ClO$_4$)$_2$ (31.6 mg) in acetonitrile (3 mL), the **L**–Hg^{2+} (4.1 mg) was then filtered out and dissolved in acetonitrile (10 mL), to give a final concentration of $6.7*10^{-4}$ M solution.

The UV-Vis absorbance of the solvent background was measured, followed by eleven dilutions of the standard Ru(bipy)$_3$ stock solution. The fluorescence emission was also measured using λ_{ex} = 452 nm and λ_{em}= 460 – 700 nm. This was repeated for the **L**–Hg^{2+} test sample, fluorescence emission was measured using λ_{ex} = 380 nm and λ_{em}= 400 – 700 nm. The integrated fluorescence intensity was plotted against the absorbance at the fluorometer excitation wavelength. This is at 452 nm for Ru(bipy)$_3$ and 380 nm for **L**–Hg^{2+}. A linear regression line was fitted to the resulting graph, of which the gradient is required for the quantum yield calculation.

Eq. S1 was used to calculate the fluorescence quantum yield. Where 'x' denotes the complex **L**–Hg^{2+} (test sample) and 'STD' denotes Ru(bipy)$_3$ (standard sample). φ represents the quantum yield, m represents the gradient of the plot of integrated fluorescence intensity vs absorbance, and η represents the refractive index of the solvent used.

$\varphi_x = 0.57$

Propagation of error for quantum yield calculations for **L–Hg^{2+}-Complex**. Eq. S2 was used to calculate the standard deviation from quantum yield.

Table S2. Variables for calculation of the standard deviation from quantum yield for **L– Hg^{2+}** complex

Parameter	Value	Standard Error (±)
Quantum Yield, ϕ_x, L-Hg(II) Complex	0.57	0.16
m_x	3.24×10^4	2.05×10^3
m_{STD}	2.03×10^4	1.31×10^3
ϕ_{STD}	0.36	0.01
$\sigma_{mx} = standard\ error\ of\ m_x * \sqrt{N}$	6.48×10^3	-
$\sigma_{mSTD} = standard\ error\ of\ m_{STD} * \sqrt{N}$	4.14×10^3	-

The standard deviation from quantum yield for L–Hg^{2+} complex was calculated using Eq. S2.

$$\sigma_x = 0.57 \sqrt{\left(\frac{6.48 \times 10^3}{3.24 \times 10^4}\right)^2 + \left(\frac{4.14 \times 10^3}{2.03 \times 10^4}\right)^2 + \left(\frac{0.01}{0.36}\right)^2} = 0.16$$

Fluorescence Emission Experiment of Hg^{2+} with Fe$_3$O$_4$@TiO$_2$-L NP

The fluorescence samples of Fe$_3$O$_4$@TiO$_2$-L NP were prepared by adding 1.0 mg of Fe$_3$O$_4$@TiO$_2$-L NP into 3.0 mL of anhydrous acetonitrile and sonicating it for 15 minutes. The solution was then transferred to a 10 mm x 10 mm quartz cuvette. The fluorescence emission was measured using $\lambda_{ex} = 330$ nm and $\lambda_{em} = 340 - 600$ nm at a slow scan rate. A stock solution of Hg^{2+} was prepared by dissolving Hg(ClO$_4$)$_2$ in acetonitrile, which was added drop wise to the solution in intervals of 1.0 µL using a microsyringe, the fluorescence spectra of the Fe$_3$O$_4$@TiO$_2$-L NP with Hg^{2+} were measured three times each to obtain the average peak height. Between each run and addition, the solution was mixed for 30 sec before the fluorescence emission was measured.

Selectivity Experiment of Hg^{2+} with Fe$_3$O$_4$@TiO$_2$-L NP

Eight metal solutions (Fe^{2+}, Fe^{3+}, Cr^{3+}, Zn^{2+}, Co^{2+}, Ru^{3+}, Cd^{2+}, and Cu^{2+}) were prepared by dissolving the corresponding metal salt in acetonitrile. 1.0 mg of Fe$_3$O$_4$@TiO$_2$-L NP was added into 3.0 mL of anhydrous acetonitrile and sonicated for 15 minutes then transferred to a 10 mm x 10 mm quartz cuvette. The fluorescence emission was measured using $\lambda_{ex} = 330$ nm and $\lambda_{em} = 340 - 640$ nm. An aliquot of the first metal solution was added to the cuvette, sonicated for 2 minutes. Then the fluorescence emission of M+L was measured. Hg^{2+} was then added to the cuvette, sonicated for 2 minutes before the UV-vis and fluorescence emission of M+L + Hg^{2+} was obtained. These steps were repeated for all seven metal salts.

Mercury uptake experiment by Fe$_3$O$_4$@TiO$_2$-L NP from aqueous solutions.

Cold Vapour atomic absorption (AA) method was employed to study mercury uptake ability for Fe$_3$O$_4$@TiO$_2$-L NP nanomaterial as previously reported.[10] In this experiment, a mass of 62.0 mg of mercury perchlorate was weighed out, and then dissolved in 100 mL of type 1 deionized water

(DI water) in a 100 mL volumetric flask to create an initial stock solution of 274 mg/L mercury. Calibration solutions and test solutions were prepared by stepwise dilution of the stock solution. Mercury uptake ability was determined in triplicates to ensure reliable measures of the uptake properties. For the mercury uptake experiment, samples were created by adding 7.5 mL of the working 1 mg/L stock solution to the 30 mL sample vials. Then 1.7-1.9 mg of $Fe_3O_4@TiO_2$-L NP were added to the vial and sonicated for 15 minutes to allow for complete exposure to the solution. Following this, the reacted $Fe_3O_4@TiO_2$-L NP material was removed from the media using a magnet, the solutions were quantitatively transferred to a 100 mL volumetric flask and diluted to 100 mL using DI water. Mercury content was measured using a Varian AAS 240 instrument equipped with a cold-vapour absorption set-up, using stannous chloride as the reductant. Mercury absorption ability of the $Fe_3O_4@TiO_2$-L NP was determined as $13.35*10^{-3}$ mg of Hg^{2+}/ mg of material or 13.35 μg Hg^{2+} /mg of material.

Table S3. Mercury uptake analysis by $Fe_3O_4@TiO_2$-L NP material.

Mercury Uptake Analysis							
Sample	Concentration Hg Initially (μg/L)	Mass of Magnetite NP's Added (mg)	Absorbtion Measured	Concentration After Addition and Removal of NP's (μg/L)	Mercury Uptake/ mg of NP's (μg/L)	Mercury Uptake (mg/mg)	Mercury Uptake (μg /mg)
1	75	1.7	0.3323	50.79	14.24	0.01424	14.24
2	75	1.9	0.3312	50.65	12.81	0.01281	12.81
3	75	1.8	0.3386	51.59	13.01	0.01301	13.03
Average	75	1.8	0.3340	51.01	13.35	0.01335	13.35

Binding constants calculations

A modified Stern Volmer equation shown below was used to calculate the binding constants

$$log\frac{F_0 - F}{F} = logK_b + nlog[Q]$$

Where F_0 is the fluorescence intensity of L at 413 and F is the intensity of L at 413 nm in the presence of Hg^{2+}. Kb is the binding constant, n is the number of binding sites (n=1 for our system) and [Q] is the concentration of Hg^{2+}.

Limit of detection calculations

The limit of detection (LOD) was calculated from the calibration curves using the following equation. Where σ is the standard deviation of the response.

$$LOD = \frac{3\sigma}{slope}$$

Electrochemistry

An ink was made by sonicating 2.7 mg of the $Fe_3O_4@TiO_2$-L NP, 100µL deionized water, 100µL isopropyl alcohol, and 50µL Nafion®. 2µL of the ink was drop coated onto a 0.071cm^2 diameter glassy carbon electrode and dried with heat (loading of the material: 304µg/cm^2). The functionalized electrode was immersed into a 0.6 mM solution of Hg^{2+} for 30 min. The electrode was washed and corresponding electrochemical tests were ran. The electrode was then immersed in a 5 mM solution of Fe^{3+} for 30 min. The electrode again was washed with water and electrochemical tests were performed.

Electrochemcial measurements were ran in 0.1M H_2SO_4. A mercury/mercury sulfate was used as a reference electrode and a platinum wire was used as the counter electrode. Cyclic voltammetry (CV) was performed at 50mV/s and 10mV/s in the potential range of 0-1.2V vs SHE. The electrochemical measurements were performed using a Solartron Analytical 1470E potentiostat with corresponding Multistat and CView software. Differential pulse voltammetry was run with a height of 50mV, width of 10ms, period of 100ms, and increment of 10mV on a Pine wavedriver with corresponding aftermath software.

References

S1.   E. C. Constable and A. M. W. C. Thompson, *J. Chem. Soc., Dalton Trans.*, 1992, 2947-2950.

S2.   P. Thapa, R. Karki, A. Basnet, U. Thapa, H. Choi, Y. Na, Y. Jahng, C.-S. Lee, Y. Kwon, B.-S. Jeong and E.-S. Lee, *Bull. Korean Chem. Soc.*, 2008, **29**, 1605-1608.

S3.   W. Goodall and J. A. G. Williams, *J. Chem. Soc., Dalton Trans.*, 2000, 2893-2895.

S4.   W.-F. Ma, Y. Zhang, L.-L. Li, L.-J. You, P. Zhang, Y.-T. Zhang, J.-M. Li, M. Yu, J. Guo, H.-J. Lu and C.-C. Wang, *ACS Nano*, 2012, **6**, 3179-3188.

S5.   H. Deng, X. Li, Q. Peng, X. Wang, J. Chen and Y. Li, *Angew. Chem.*, 2005, **117**, 2842-2845.

S6.   J. Yu, Y. Su, B. Cheng and M. Zhou, *J. Molec. Catal. A.*, 2006, **258**, 104-112.

S7.   J. Choudhury, R. Kaminker, L. Motiei, G. d. Ruiter, M. Morozov, F. Lupo, A. Gulino and M. E. v. d. Boom, *J. Am. Chem. Soc.*, 2010, **132**, 9295-9297.

S8.   A. T. R. Williams, S. A. Winfield and J. N. Miller, *Analyst*, 1983, **108**, 1067-1071.

S9.   K. Rurack, in *Standardization and Quality Assurance in Fluorescence Measurements I: Techniques*, ed. U. Resch-Genger, Springer Berlin Heidelberg, Berlin, Heidelberg, 2008, pp. 101-145.

S10.   G. Xiang, L. Li, X. Jiang, L. He and L. Fan, *Anal. Lett.*, 2013, **46**, 706-716.