Thiophene-based fluorescent mercury sensors

Austin K. Shigemoto, Carolyn N. Virca, Samuel J. Underwood, Lauren R. Shetterly and Theresa M. McCormick

Department of Chemistry, Portland State University, Portland, OR, USA

ABSTRACT
Coordination chemistry of thiophene rings is poorly understood, despite their common use in organic electronic materials. The absorption and emission responses to transition metal ions of three thiophene-based ligands containing pyridine chelating groups are examined. These ligands, 2-(2'-thienyl)-pyridine (L1), 2,5-bis(2-pyridyl)thiophene (L2), and 2,6-bis(2-thienyl)pyridine (L3), show a ratiometric fluorescence response in the presence of Hg(ClO4)2 with reasonable selectivity against many transition metal ions in acetonitrile. 1H NMR data support S,N chelation of L1 and L2 to the Hg(II) center, while L3 coordinates through cyclometalation via one carbon of thiophene. DFT calculations suggest thiophene coordinates to Hg(II) in a bent geometry. Our results indicate that thiophene could offer selectivity for Hg(II) towards the design of fluorescent sensors.

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1. Introduction
The coordination chemistry of heterocyclic aromatic ligands has been studied for a wide variety of applications including catalysts, photosensitizers, and molecular sensors [1–5]. Ligands such as pyridine or N-heterocyclic carbenes have been studied extensively [6–9]. In contrast, thiophene coordination chemistry is poorly understood. The few examples of thiophene coordination in the literature focus on metal-catalyzed hydrodesulfurization [10]. The photo-electronic properties of polythiophenes and thiophene containing small molecules are extensively studied for use in organic photovoltaic devices (OPVs) [11–14], yet the ability of sulfur in thiophene to coordinate to metals has not been fully explored. To increase efficiency in OPV applications it is necessary to increase device absorption in the red to near-infrared (NIR) region [11, 15–20]. Metal coordination provides a potential avenue to red-shift
absorption and enhance the electronic properties of these materials. Also, as a molecular sensor, sulfur of thiophene could offer selectivity for the detection of soft heavy metals such as mercury(II) or lead(II).

Existing crystal structures of coordinated thiophene ligands display a number of different coordination modes including η^1(S) sulfur-coordination, η^1(C) carbon-coordination, η^2 through two carbon atoms, η^4 through four carbon atoms, or η^5 through all atoms in the cyclic ring [10, 21-27]. To the best of our knowledge carbon coordination in the 2-position of the thiophene is the most commonly observed coordination mode for thiophene ligands [26–37]. In contrast, sulfur-coordination is rarely observed, likely due to resonance effects placing a positive charge along the sulfur and delocalizing a negative charge along the carbons [21–23, 38]. The coordination of thiophene is dependent on both the functionalization of the ring as well as the transition metal [10, 38–40]. The effect of thiophene coordination on the photophysics of the ligand has not been reported.

Herein, we report several thiophene-based ligands substituted with pyridine groups to facilitate sulfur-coordination (figure 1). We speculate that pyridine should enhance sulfur coordination both through chelation and increasing the electron density on the thiophene. Metal coordination has been studied using absorption, emission and NMR spectroscopy. Based on density functional theory (DFT) calculations, we propose that mercury coordinates through S-N chelation for these ligands. Additionally, the ligands show selectivity towards mercury as evidenced by their absorption and emission responses, making them potentially viable as fluorescent mercury sensors.

2. Experimental

2.1. Materials and methods

Reagents were obtained from Sigma Aldrich and TCI America Chemicals and used without purification. The ligand 2-(2′-thienyl)-pyridine (L1) was obtained from TCI Chemicals and further purified by recrystallization in hexanes. Acetonitrile (CH₃CN), acetone, hexanes, tetrahydrofuran (THF), dichloromethane, diethyl ether (Et₂O), chloroform, ethyl acetate, and metal salts were obtained from Sigma Aldrich. 1,4-Dioxane was obtained from TCI America Chemicals. The identity of organic compounds was confirmed by ¹H NMR spectroscopy performed with a Bruker-Avance III 400 MHz spectrometer with a 9.4 Tesla magnet and a 5 mm BBO probe. Mass spectra were recorded on a Thermo Electron LTQ-Orbitrap Discovery high-resolution mass spectrometer. Emission spectra and quantum yields were obtained using a PTI Quantamax 300 Phosphorimeter with a Xe-flash lamp and PMT detector. Quantum yields were obtained using a PTI K-sphere “petite” integrating sphere. Absorption spectra were collected on a UV-3600 Shimadzu UV–vis NIR spectrophotometer.

2.2. Synthetic methods

2.2.1. Preparation of 2,5-bis(2-pyridyl)thiophene (L2)

A flask containing 2,5-thiophenediylbisboronic acid (0.402 g, 2.33 mmol, 1 eq), cesium carbonate (1.63 g, 4.99 mmol, 2 eq) and tetrakis(triphenylphosphine)palladium(0) (0.020 g, 0.017 mmol, 0.01 eq) was purged with N₂ gas before the addition of 2-bromopyridine (0.500 mL, 5.24 mmol, 2.2 eq), 1,4-dioxane (10 mL) and water (5 mL). Solvents and 2-bromopyridine were purged of air prior to addition by three freeze-pump-thaw cycles. The yellow solution was heated to 105 °C and left stirring overnight.

Figure 1. Structural depiction of L1–L3.
After the reaction cooled to room temperature, 10 mL of water was added. The product was extracted in CH2Cl2 (3 × 40 mL). The organic layers were combined and dried with Na2SO4. The filtered solvent was evaporated in vacuo to afford a yellow–orange solid. The crude product was purified by silica gel column chromatography, eluted with 50 : 50 ethyl acetate : hexanes. The final product was obtained as a yellow solid (0.207 g, 37.1% yield) and characterized via 1H and 13C NMR spectroscopy (CD3CN 450 MHz) δ (ppm): δ 8.60 (d, J = 4.0, 1H), 7.74–7.65 (m, 2H), 7.64 (s, 1H), 7.15–7.18 (dd, J = 6.4, 4.9 Hz, 1H) 13C NMR (101 MHz, CD3CN) δ 151.85, 149.20, 146.03, 136.63, 125.47, 122.16, 118.44. FTMS + p ESI Calcd for C14H10N2S, 239.06374; found, 239.06560.

2.2.2. Synthesis of 2,6-bis(2-thienyl)pyridine (L3)
A flask containing 2,6-dibromopyridine (0.482 g, 2.03 mmol), thiophene-2-boronic pinacol ester (0.882 g, 4.19 mmol), potassium fluoride dihydrate (0.351 g, 6.04 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.082 g, 0.064 mmol) was purged with N2. A solution of 1,2-dimethoxyethane (20 mL) and water (15 mL) was degassed by three freeze-pump-thaw cycles and added. The flask was sealed and heated to reflux for 4 h. The organic layer was then removed in vacuo and 50 mL of water was added. The product was extracted in Et2O (3 × 50 mL), the organic layers combined, and then washed with water (1 × 50 mL). The organic layer was dried over Na2SO4 and the solvent was evaporated to afford an orange oil. The crude product was then purified by column chromatography, eluted with 50 : 50 CHCl3 : hexanes. The final product was obtained as a white solid (0.0814 g, 16.4% yield) and characterized by 1H and 13C NMR spectroscopy. 1H NMR (CD3CN 450 MHz) δ 7.79 (dd, J = 8.4, 7.3 Hz, 1H), 7.71 (d, J = 3.7 Hz, 2H), 7.65 (d, J = 7.7 Hz, 2H), 7.52 (d, J = 5.1 Hz, 2H), 7.16 (dd, J = 5.1, 3.7 Hz, 2H). 13C NMR (101 MHz, CD3CN) δ 151.84, 137.83, 128.17, 128.07, 125.03, 116.79. FTMS + p ESI Calcd for C13H9NS2, 244.02492; found, 244.02667.

2.3. General procedure for absorption/emission titrations
Ligand solutions of 1 × 10−5 M L1, L2, and L3 were prepared in CH3CN. The metal salts solutions of Fe(ClO4)3 and Hg(ClO4)2 were prepared fresh the day of the experiment at 0.02 M concentration in 1 × 10−5 M L1 solution to preserve the concentration of ligand throughout the titration. Metal salt solutions for titrations with L2 and L3 were prepared at 0.20 M concentration in 1 × 10−5 M solution of either L2 or L3. After an initial spectrum of the ligand was obtained, increasing molar equivalents of the metal salts were added to the solution, via micropipette, until no change in the spectra were observed.

2.4. General procedure for 1H NMR titrations
1H NMR titrations were performed by preparing 4 × 10−3 M ligand solutions in CD3CN. Initial 1H and COSY NMR spectra of the ligand were obtained prior to addition of a metal salt. Increasing equivalents of the metal salt were added to the solution. 1H NMR spectra were obtained. COSY spectra were used to assign the peaks of the complexes.

2.5. General procedure for metal competition
Solutions of silver(I), cadmium(II), cobalt(II), copper(II), iron(II), iron(III), magnesium(II), manganese(II), sodium(I), nickel(II), lead(II), and zinc(II) perchlorates (0.02 M) and L1–L3 (1 × 10−5 M) were prepared in CH3CN. An emission spectrum was obtained for the ligand solution. Metal perchlorate (5 eq) was added to a 10 mL aliquot of 1 × 10−5 M ligand solution and an emission spectrum was obtained after 5 min of stirring. Then 5 eq of Hg(ClO4)2 was added to each solution and stirred for 5 min before another emission spectrum was obtained.
2.6. Computational chemistry

DFT calculations were run using Gaussian 09 [41] with the B3LYP [42, 43]/6–311 + G(d) for all atoms but Hg, which was run with the LanL2DZ basis set. Optimizations and TD–DFT calculations were performed for Hg(L1)(ClO4)2, L1–L3. The full width at half max for Gaussian functions used in the generated UV–vis spectra was 0.3 eV.

3. Results and discussion

3.1. Ligand synthesis and structure

Three ligands with thiophene and pyridine coordination sites were studied. L1 has one thiophene and one pyridine (figure 1). We hypothesize that pyridine will coordinate to transition metals and hold the thiophene in close proximity to the metal, thereby facilitating sulfur coordination. L2 (central thiophene with two flanking pyridine groups) and L3 (central pyridine with two flanking thiophene groups) were synthesized using modified literature procedures [44, 45] and were designed to have several coordination sites in a larger π-conjugated system to increase sensitivity and red-shift the absorption and emission properties (figure 1). Previous attempts to coordinate L3 to chromium(II), cobalt(II), nickel(II), copper(II), silver(II), and zinc(II) were unsuccessful [44]. To the best of our knowledge these ligands have not been shown to coordinate to mercury(II).

The structures of all three ligands were verified by 1H, 13C NMR and MS. DFT calculations were performed on each of the ligands. Optimized structures of the ligands show that they are planar compounds. The dihedral angles measured from the optimized structures of the ligands are nearly planar (angles: L1 – S–C–C–N, 179.98°; L2 – N–C–C–S, 179.98°; L3 – S–C–C–N, 179.99°). The heteroatoms in each of the rings rotate as shown in figure 2 to prevent ortho-hydrogen interactions.

3.2. Photophysical properties of ligands

Absorption and emission spectra of L1–L3 were obtained with 1 × 10−5 M solutions in CH3CN (figure 3). Absorption spectra of both L2 and L3 are red-shifted relative to L1 due to extended conjugation from the additional ring. The lowest energy absorption maximum of L1 is at 298 nm; L2 and L3 have peaks at 342 and 335 nm, respectively (table 1). Likewise the emission of both L2 (λmax = 394, Φ = 0.56) and L3 (λmax = 376, Φ = 0.34) are red-shifted compared to that of L1 (λmax = 356 nm, Φ = 0.43). Extending the conjugation to three rings pushes the emission into the visible region, providing easy detection of metal binding through visual inspection. The lower energy absorption and emission of L2 relative to L3 is likely due to the more bent structure of L3 caused by the geometry of the central pyridine (figure 2).

Measured absorbance spectra are consistent with excitation energies calculated by TD-DFT (see Supporting Information). The calculated lowest energy absorption for L1 is at 338 nm and the calculated lowest energy absorption for L2 is red shifted to 355 nm. For both L1 and L2 the lowest energy excitation is HOMO to LUMO in nature. The lowest energy peak in calculated absorption spectra of L3 comprises three transitions at 332, 314, and 290 nm. All three excitations are combinations of the HOMO−1 and HOMO to the LUMO and LUMO + 1 (depicted in the Supporting Information). Likewise, three excitations are seen in the measured absorption spectra of L3.

| Table 1. Summary of photophysical properties of L1–L3, and the complexes formed in solution with Hg(ClO4)2. |
|-----------------|----------|-----------|----------|----------|----------|----------|
| L1              | λabs (nm) | ε (× 104, M⁻¹, cm⁻¹) | λex (nm) | λem (nm) | Φ (%)    |
| Hg(L1)(ClO4)₂   | 298      | 1.50      | 304      | 356      | 42       |
| Hg(L2)(ClO4)₂   | 335      | 1.71      | 344      | 410      | 79       |
| L2              | 342      | 2.90      | 343      | 394      | 56       |
| Hg(L2)(ClO4)₂   | 369      | 2.27      | 374      | 435      | 54       |
| L3              | 284      | 2.00      | 291      | 376      | 34       |
| Hg(L3)(ClO4)₂   | 380      | 1.78      | 377      | 457      | 48       |
3.3. Interaction with mercury in solution

3.3.1. Photophysical response to mercury

In the presence of mercury ions (Hg(ClO$_4$)$_2$), the absorption and emission spectra of all three ligands red-shift. With increasing equivalents of Hg(II), the ligand-based absorption decreases and a new, red-shifted absorption grows in. For $L_1$, the absorbance at 298 nm decreases while a peak at 322 nm grows until 50 equivalents of Hg(II) have been added (figure 4(a)). An isosbestic point is observed at 314 nm. Likewise, the emission of $L_1$ at 356 nm is quenched with addition of Hg(II) and a new peak at 411 nm ($\Phi = 0.79$) appears (figure 4(b)).

Although $L_2$ displays a similar red-shift in both absorption and emission, several distinct features are noted. With increasing amounts of Hg(II), $\lambda_{\text{max}}$ of the absorption at 342 nm decreases as a new peak at 368 nm increases until 20.0 eq of Hg(II) have been added (figure 4(c)). Similarly, a new emission at 446 nm ($\Phi = 0.55$) is observed (figure 4(d)). Further additions of Hg(II) past 20.0 eq cause a blue shift in absorption to 360 nm and in emission to 421 nm ($\Phi = 0.22$) (see Supporting Information). A clear isosbestic point is not observed for $L_2$ suggesting the formation of more than one new species in solution.

Addition of Hg(II) to $L_3$ also causes a red-shift in both the absorption and emission, however 100 eq of metal are required to reach saturation (figure 4(e), (f)). An isosbestic point at 344 nm indicates that no intermediate forms during the reaction. For all three compounds, addition of excess Hg(II) is required to completely quench ligand emission. The emission of the complexes also have higher quantum yield than the free ligand. Likely, this results from suppression of nonradiative decay pathways caused by decreased rotation around the single bond connecting the rings due to metal chelation. The bathochromic shift is likely due to a conformational change of the ligand to a more rigid structure.

3.3.2. NMR titration for structure determination

In order to elucidate the structure of the $L_1$-$L_3$/Hg(II) complexes, formation of the complexes were monitored using $^1$H NMR during the metal titrations into solutions of each ligand (figure 5(a)–(c)). COSY spectra were obtained at the end of each titration to assign peaks. Downfield shifts for ligand peaks...
were attributed to deshielding of the protons due to metal coordination [46]. The positive charge is delocalized on the rings such that the protons para to the Hg(II) coordination site are most deshielded. Initial addition of Hg(II) to all ligand solutions caused downfield shifts for all peaks in each spectrum.

In the case of \( L_1 \) the para proton on the pyridyl group (\( H_e \)) (figure 5(a)) shifts 0.717 ppm with addition of 2 eq of Hg(II), suggesting nitrogen coordination. H C in the three-position of thiophene was shifted 0.457 ppm relative to the free ligand suggesting possible sulfur-coordination to Hg(II). These results are consistent with S,N chelation of \( L_1 \) to Hg(II).

Since two new products are formed with addition of Hg(II) to \( L_2 \), emission spectroscopy was used in conjunction with \(^1\)H NMR to differentiate the two products. The symmetry of the molecule was retained during the titration, as evidenced by retention of the singlet peak from \( H_e \) on the thiophene (figure 5(b)). After 1.00 eq of Hg(II) was added, emission spectroscopy confirmed the identity of the first product (\( \lambda_{max} = 435 \text{ nm} \)). A low downfield shift (\( \Delta \text{ppm} = 0.083 \text{ ppm} \)) is observed for the protons at the 3,4-positions of thiophene (\( H_e \)), while a 0.471 ppm shift was observed for the proton para to the pyridyl nitrogen (\( H_c \)) (figure 5(b)). After 5 eq an emission at 420 nm indicated the second product had formed in solution. A greater downfield shift for all peaks was observed. Though it is evident that pyridine chelation occurs, the identity of the products formed in solution between \( L_2 \) and Hg(II) is unclear. The minimal shift observed for the singlet from the proton on the thiophene would indicate sulfur coordination does not occur until the second product is formed in solution. Further investigation into the structures of the two products formed for \( L_2 \) are currently underway.

During the titration of \( L_3 \) with Hg(II), a broadening of all peaks was observed until 5.00 eq of Hg(II) were added and the product was formed. Unlike titrations with \( L_1 \) and \( L_2 \), the total number of aromatic protons decreased by one after the addition of Hg(II). Another distinct feature is an apparent break in symmetry observed by an increase in the number of proton environments (figure 5(c)). Following addition of 5 eq of Hg(II), the \(^1\)H NMR spectrum suggests a proton at the three-position of one of the thiophenes had been removed from the ligand. Removal of this proton indicates S,N,C-chelation by \( L_3 \) to Hg(II). This is the only ligand that appears to coordinate through a carbon rather than sulfur.

### 3.3.3. Calculated structure

DFT structure optimization was used to explore the coordination geometry of Hg(II) with \( L_1 \). The optimized structure shows S,N-chelation to Hg(II) with the sulfur on the thiophene coordinating in a side on manner (see Supporting Information). This causes \( L_1 \) to twist so that the N and S are on the same side with a N–C–C–S dihedral angle of 41.2°. The lowest energy excitation for the calculated absorption
spectrum from the optimized geometry is red shifted to 349 nm compared to \( \text{L1} \) (\( \lambda_{\text{max}} = 338 \) nm), consistent with experiment. The orbitals involved in the absorption of the complex formed between \( \text{L1} \) and \( \text{Hg(ClO}_4)_2 \) involve a mix of metal centered and ligand centered orbitals (see Supporting Information).

### 3.4. Selectivity towards mercury

The selectivity of the fluorescent response was tested against other metal perchlorate salts: \( \text{Hg(II)} \), \( \text{Ag(I)} \), \( \text{Cd(II)} \), \( \text{Co(II)} \), \( \text{Cu(II)} \), \( \text{Fe(II)} \), \( \text{Fe(III)} \), \( \text{Mg(II)} \), \( \text{Mn(II)} \), \( \text{Na(I)} \), \( \text{Ni(II)} \), \( \text{Pb(II)} \), and \( \text{Zn(II)} \). The emissions of solutions with 5 eq of each metal salt were measured. For \( \text{L1} \), only addition of \( \text{Hg(II)} \), \( \text{Cu(II)} \), and \( \text{Fe(III)} \) resulted in an emission response. The presence of other metal ions in solution did not affect the emission response to \( \text{Hg(II)} \), with the exception of \( \text{Fe(III)} \) which showed an enhanced emission (figure 6(a)). Similar selectivity was observed for \( \text{L2} \). There is a bathochromic shift for 5 eq of \( \text{Fe(III)} \) (\( \lambda_{\text{max}} = 420 \) nm) relative to the free \( \text{L2} \). However, addition of \( \text{Hg(II)} \) alone results in a different emission (\( \lambda_{\text{max}} = 446 \) nm) (figure 6(b)). Notably, \( \text{L3} \) emission was only minorly quenched in response to 5 eq of all metal salts, including \( \text{Hg(II)} \). \( \text{Fe(III)} \) addition caused a new emission at 457 nm (see Supporting Information) (figure 6(c)). These results indicate that thiophene containing fluorescent sensors can display selectivity for \( \text{Hg(II)} \).

### 4. Conclusion

We have developed three new thiophene-based ligands with a fluorescence response to \( \text{Hg(II)} \) via chelation to the metal center. The addition of pyridyl groups enhances coordination of thiophene via chelation, as is evident through the decreased amount of \( \text{Hg(II)} \) needed to reach equilibrium with \( \text{L2} \), which contains two pyridines, relative to the amount needed to reach equilibrium with \( \text{L1} \) and \( \text{L3} \), which both contain only one pyridine. This suggests that the sulfur of thiophene is not a strong coordinating
group. $^1$H NMR suggests a S,N,C-chelation of L3 to Hg(II). Our results indicate that thiophene ligands offers selectivity for Hg(II). A unique coordination chemistry is observed for L2 and Hg(II), forming two distinct products dependent on the amount of Hg(II) in solution. Currently our lab is researching the identity of these products towards the design of thiophene-based molecular sensors. In conclusion, we have shown that thiophene containing ligands display selectivity for Hg(II) giving a visible, ratiometric fluorescence response.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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