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CH_3SCH_3 Detector
Spoiled
Fresh!?
Fresh

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ARTICLE TYPE

Chemodosimetric Analysis in Food-Safety Monitoring: Design, Synthesis, and Application of Bimetallic Re(I)-Pt(II) Complex for Detection of Dimethyl Sulfide in Foods

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Detection of neutral biogenic sulfides plays a crucial role in food safety. A new heterobimetallic Re(I)-Pt(II) donor-acceptor complex — $[Re(biq)(CO)_3(CN)]$–$[Pt(DMSO)(Cl)_2]$ (**1**, *biq* = 2,2′-biquinoline) was synthesized and characterized. The X-ray crystallographic and photophysical data for **1** are reported in this study. Complex **1** indicated the luminescent chemodosimetric selectivity for dimethyl sulfide, which persisted even in the presence of a variety of interfering vapors, with a detection limit as low as 0.96 ppm. The binding constant (log K) of **1** toward dimethyl sulfide was 3.63 ± 0.03. The analyte selectivity of the complexes was found to be dependent on the ligand coordinated to the Re(I) center. Real samples (beef, chicken, and pork) were monitored real-time for gaseous dimethyl sulfide. Complex **1** shows a linear spectrofluorimetric response with increasing storage time of the meats at 30 °C.

Introduction

Practical and cost-effective detection of food freshness is a long-standing challenge in our modern society. With technological advancements and tightened regulatory controls, food safety is seemingly guaranteed. However, there are still many cases of food poisoning, which undermine consumer confidence and have untold financial, political, and health costs. The Center for Disease Control and Prevention of the USA estimates that, from 2000–2007, 50 million Americans suffered from food poisoning due to food-borne illnesses, resulting in 3,000 deaths and 130,000 hospitalizations.[1a–b] Public concerns over food safety are escalating. Consumers need to be assured of the safety of the food products they are buying. However, ordinary food-safety tests are generally tedious and slow, and problems are usually identified after contaminated/rotten food items have been sold or even consumed. Therefore, scientific approaches to determining the level of contaminants in food and beverage products are highly desirable.

Food spoilage is an enormous problem for food industries. During spoilage, organic food components such as proteins, lipids, and lignin convert to low-molecular-weight compounds known as biogenic volatile compounds (BVCs) and generate putrid odors. Thus, biogenic sulfides, amines, and carboxylic acids are key markers of food quality.[1c–e] In particular, biogenic sulfides such as dimethyl sulfide, disulfide, and trisulfide are important indicators of the quality of meat, egg, and dairy products.[2] The spoilage of meats and dairy foods generates a rancid smell. The concentration of biogenic sulfides can increase by a thousand times, up to ppm levels, in the headspace of spoiled poultry when it is improperly stored,[2d] but the safety regulations enable up to 2 ppm.[2e] Overexposure to these chemicals can cause nausea, headache, dizziness, and vomiting.[2f,g]

Currently, the reported methods for detecting biogenic sulfides require analytical instruments such as GC-MS, LC-MS, or electronic sensor arrays.[3] However, these manipulative and instrumental procedures are tedious and time-consuming. Although the general public needs to be ensured of food safety in a fast and facile manner, there are ***no*** published examples of molecular probes for these biogenic sulfides. Despite a plethora of literature on detecting thiol compounds (R–SH), there are no examples of molecular probes for CH_3SCH_3, CH_3SSCH_3, and CH_3SSSCH_3.[4]

Traditional chemosensors are developed for molecular detection.[5-9] Unfortunately, this approach is limited in the area of food safety by the reversibility of the sensing properties. As a result, increasing attention is now being paid to the use of chemodosimeters, which are molecular devices that react with analytes and yield physical signals in an irreversible fashion.[10] In contrast to chemosensors, which count the analyte in real-time, chemodosimeters react with the analyte in a cumulative fashion.[9,10] This property makes chemodosimeters especially suitable for food-quality monitoring.[9f] Because the signal from the chemodosimeter that indicates spoilage cannot be reversed, operators/customers can undoubtedly recognize that contamination has occurred regardless of which stage of food processing it occurs. However, detection of neutrally charged BVCs through chemodosimetric methods is difficult. Because the neutral compounds generally have low nucleophilicity and electrophilicity and are present at low concentrations with many interfering odors, few examples of molecular probes for them have been found, especially compared to the number reported for charged molecules. Thus, chemodosimeters that can selectively and sensitively detect BVCs and be applied in practical situations are highly desirable.

In this work, the feasibility of using bimetallic donor-acceptor ensembles (BmDAEs) as chemodosimeters to determine the presence of dimethyl sulfide is explored. Through molecular

design, a Re(I) metallic indicator (donor) was linked to a Pt(II) metallic receptor (acceptor) via a supramolecular interaction to form a BmDAE. Upon introduction of the competitive dimethyl sulfide molecule into the system, the sulfide coordinates with the receptor and displaces the indicator, which produces an optical signal. The ensembles produce naked-eye luminescent responses specific to dimethyl sulfide down to 0.96 ppm in real swine, beef, and chicken-loin samples.

Experimental Section[10]

Synthesis and characterization

[Re(*biq*)(CO)$_3$(CN)]–[Pt(DMSO)(Cl)$_2$] **(1).** Complex **1** was formed by stirring Pt(DMSO)$_2$Cl$_2$ (0.0844 g, 0.2 mmol) with one equivalent of Re(*biq*)(CO)$_3$(CN)[11] (0.110 g, 0.2 mmol) in a methanol/chloroform mixture (1:1, 150 mL) under ambient atmosphere at room temperature for 30 min. The solution was reduced to dryness *in vacuo* and the crude product obtained was extracted several times with MeOH. Yellow-orange crystalline plates of **1** were obtained by slow diffusion of diethyl ether into a CH_2Cl_2 solution of **1**. Yield: 84% (0.15 g). The new complex was characterized by X-ray crystallography, ^{1}H NMR, ESI-MS, IR spectroscopy, TLC analysis, and microanalysis. (400 MHz, $CDCl_3$) δ ppm = 8.81 (d, J = 9.2 Hz, 2H), 8.57 (d, J = 8.8 Hz, 2H), 8.47 (d, J = 8.8 Hz, 2H), 8.00 (d, J = 8.4 Hz, 4H), 7.80 (t, J = 7.6 Hz, 2H), 3.19 (s, 6H) . IR (KBr): $\nu_{C\equiv N}$ = 2169 cm^{-1}; $\nu_{C\equiv O}$ = 2022 and 1903 cm^{-1}. ESI-MS (+ve mode): m/z 919.5 {[Re(*biq*)(CO)$_3$(CN)]–[Pt(DMSO)Cl$_2$]•Na}$^+$. TLC: silica gel and ethyl acetate/MeOH (3:1), Rf = 0.7. Anal. Calcd. for $C_{24}H_{18}Cl_2N_3O_4PtReS$: C, 32.14; H, 2.02; N, 4.69. Found: C, 32.11; H, 2.00; N, 4.67.

UV-Vis Spectroscopic and Spectrofluorimetric Titrations

All solvents used for UV-Vis absorbance and spectrofluorimetric titrations were of analytical grade. The titrations were performed in chloroform, and the measurements were recorded after equilibrium was established between the receptor and substrate. The receptor-substrate interaction was determined to be 1:1 according to the Benesi-Hildebrand equations[11] for UV-Vis absorption titration.

Detection of Gaseous Dimethyl Sulfide in Swine Sample using Complex 1

A 0.5 kg fresh swine loin was purchased from a local market and homogenized in a food processor. Immediately after, a series of 20 g of homogenized meat samples spiked with dimethyl sulfide (0–150 ppm; sets 1a–g); a mixture of dimethyl sulfide and BVCs (dimethyl disulfide, dimethyl trisulfide, CO, triethylamine, propanoic acid, 4-ethylphenol, and CH_4; each of those is 150 ppm; set 2); each BVC used in set 2 except dimethyl sulfide (150 ppm; sets 3–9); and a mixture of the BVCs used in sets 3–9 (each of them at 150 ppm; set 10) were sealed in 40 mL glass containers. These samples were held at room temperature with gentle shaking for 15 min. Gaseous vapor (6.0 cm^3) was sampled from the headspace of the container and injected into a 2.0 mL chloroform solution of **1** (1×10^{-4} M). After reaching equilibrium after 45 min, the luminescent responses (I/I_0) of **1** were recorded as a function of the spiked concentration.

Luminescent Response of Complex 1 toward Cattle, Swine, and Poultry Samples stored at 4 and 30 °C

The dosimetric properties of **1** toward swine, cattle, and poultry samples were determined by studying the luminescent responses (I/I_0) of the complex as a function of time. Homogenized meat (75 g) was sealed in a 120 mL glass container. The samples were stored at two different temperatures: 30 and 4 °C. After the set storage time, gaseous vapor (6.0 cm^3) from the headspace of the meat container was removed and injected into 2.0 mL of a chloroform solution of **1** (1×10^{-4} M). After equilibrium was reached after 45 min, the luminescence (I/I_0) of **1** were recorded as a function of time.

Results and Discussion

Synthesis of Heterobimetallic Complex 1

A neutral Re(I)-based bimetallic complexes was synthesized as a chemodosimeter for dimethyl sulfide. Through control of the thermodynamics of Re(I), Pt(II), and the organic ligands, the selectivity, sensitivity, and detection limits of the BmDAEs toward BVCs were manipulated. Complex **1** was capable of acting as a selective chemodosimeter for dimethyl sulfide.

Complex **1** was formed by stirring one equivalent of Pt(DMSO)$_2$Cl$_2$ with one equivalent of Re(*biq*)(CO)$_3$(CN) in a methanol/chloroform mixture (1:1) in an open atmosphere at room temperature (Scheme S1)[11]. The complex was isolated as air-stable yellow to yellow-orange crystalline solids in reasonable yields (84%). This neutral complex is soluble in organic solvents such as DMSO, DMF, acetonitrile, chloroform, and dichloromethane, but is virtually insoluble in water. The integrity of the donor–acceptor adduct in such a medium is demonstrated by its electrospray-MS peaks: {[Re(*biq*)(CO)$_3$(CN)]–[Pt(DMSO)Cl$_2$]•Na}$^+$ at 919.5 m/z (Fig. S4). Formation of the cyano-bridged heterobimetallic complex was also confirmed by IR spectroscopic analysis: the $\nu_{C\equiv N}$ of crystalline complex **1** shifted to higher energies from those of their *fac*-[Re(*biq*)(CO)$_3$(CN)] precursors (Table S1). Complex **1** as well as it *fac*-[Re(*biq*)(CO)$_3$(CN)] precursors were also characterized by ^{1}H NMR spectroscopy (Fig. S7–8) and gave satisfactory elemental analyses. The crystal structure of **1** was determined by X-ray crystallography.[10]

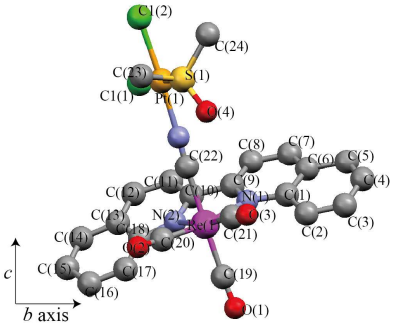

Figure 1. View of [Re(*biq*)(CO)$_3$(CN)]–[Pt(DMSO)(Cl)$_2$] (**1**) along the *a* axis showing adopted numbering scheme. Hydrogen atoms are omitted for clarity. (Pt in orange; Re in purple; C in grey; O in red; N in blue; S in yellow, Cl in green).

Electronic Absorption and Luminescent Properties of 1

The UV-Vis absorptions and spectrofluorometric properties of the Re(*biq*)$(CO)_3$(CN) chromophores before and after coordination of the Pt(DMSO)Cl_2 acceptor are compared and tabulated in Table S4. The absorption maxima of the [dπ(Re)→π*(diimine)] metal-to-ligand charge-transfer (MLCT) transitions[12] of Re(*biq*)$(CO)_3$(CN) is observed at 431 nm in chloroform at 298 K. Upon coordination of the Pt(DMSO)Cl_2 acceptor, the MLCT transitions of the complex shift to higher energies of 426 nm. Complex **1** gives a relatively strong orange emission compared to that of its precursor, Re(*biq*)$(CO)_3$(CN), in chloroform at 298 K. The emission maximum of the [π*(diimine)→dπ(Re)] ^{3}MLCT of Re(*biq*)$(CO)_3$(CN) is observed at 675 nm. Upon coordination of the Pt(DMSO)Cl_2 acceptor, the ^{3}MLCT emission of **1** blue-shifts to 651 nm and is significantly enhanced.[13] All the spectral experiments were repeated in acetonitrile at room temperature. As expected for charge-transfer transitions, the absorption and emission spectra are solvent-dependent. The charge-transfer band maximum of Re$(CO)_3$(*biq*)(CN) shifts from 420 nm in acetonitrile (more polar) to 431 nm in chloroform (less polar); in contrast, the solvent sensitivity is significantly reduced in the cyano-bridged binuclear complex (the absorption maxima of complex **1** are 423 and 426 nm in acetonitrile and chloroform, respectively).

Chemodosimetric Responses of Complex 1 toward Gaseous Biogenic Sulfide

The spectroscopic properties of complex **1** in chloroform solution at room temperature are perturbed by the presence of dimethyl sulfide. The results of UV-Vis absorption and spectrofluorometric titrations of complex **1** with dimethyl sulfide are shown in Figures 2a and b. Upon the addition of dimethyl sulfide to **1**, the MLCT transitions of the complex shift from 413 to 427 nm (Figure 2a) while the ^{3}MLCT emissions remain at 651 nm with a significant quenching in intensity (Figure 2b). The formation constant (log $K_{overall}$) of complex **1** toward dimethyl sulfide was determined to be 3.63 ± 0.03 by fitting the titration curves with the 1:1 Benesi-Hildebrand equation[11] (Figure 2c). This suggests that the Pt(II) center in complex **1** binds one molecule of dimethyl sulfide. Figure 2d summarizes the spectrofluorimetric titrations of complex **1** (1.0×10^{-4} M) with common BVCs including dimethyl sulfide and others such as dimethyl disulfide, dimethyl trisulfide, triethylamine, propanoic acid, 4-ethylphenol, N_2, CO, CH_4, and N_2. Among all the gases, only those with mono-sulfide functionality, such as CH_3SCH_3, induce a spectrofluorometric response. Other common moieties, including disulfide (CH_3SSCH_3) and trisulfide (CH_3SSSCH_3), did not induce observable spectrofluorometric changes. We also found that the spectroscopic and spectrofluorimetric responses of complex **1** toward hydrogen sulfide, H_2S, are similar to those of dimethyl sulfide (log $K_{overall}$ of complex **1** toward H_2S was determined to be 3.81 ± 0.005, Fig. S13). Thus, complex **1** responds solely to the mono-sulfide functionality (RSR where R = H or alkyl group). The sensitivity of the complex toward CH_3SCH_3 in the luminescent mode of detection (3:1 signal to noise ratio) was found to be 0.96 ppm.

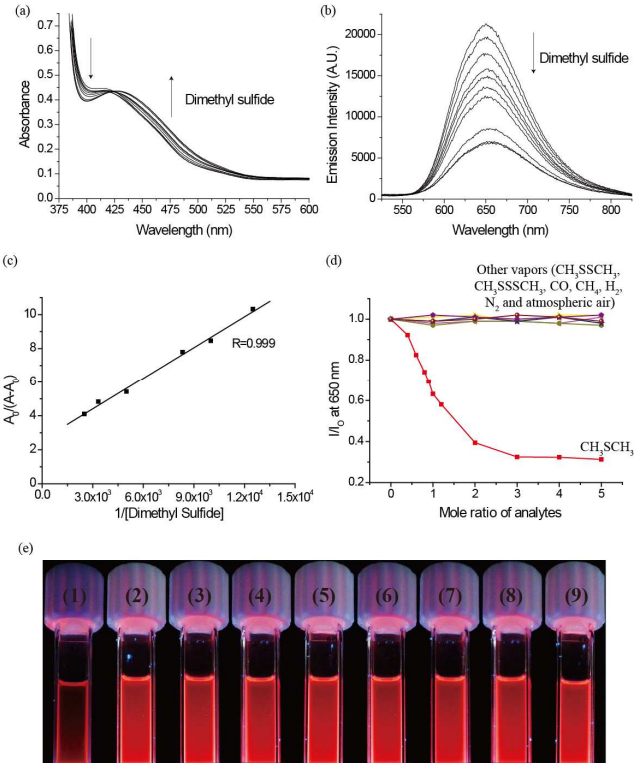

Figure 2. (a) UV–Vis absorption spectra and (b) spectrofluorimetric titrations of complex **1** (1×10^{-4} M) with CH_3SCH_3 (0 to 5×10^{-4} M) (λ_{ex} = 432 nm). (c) Plot of $A_0/(A-A_0)$ versus 1/[dimethyl sulfide]: Slope and y-intercept of the best-fit line are 6.06×10^{-4} M and 2.589, respectively, log K = 3.63 ± 0.03 at 460 nm. All titrations were carried out in $CHCl_3$ at 298 K. (d) Summary of spectrofluorometric titration (I/I_0 at 650 nm) of complex **1** (1.0×10^{-4} M) with various analytes as a function of their increasing concentration (λ_{ex} = 432 nm). (e) Photos of luminometric responses of complex **1** (1.0×10^{-4} M) in $CHCl_3$ at 298 K. (*1*) **1** + CH_3SCH_3; (*2*) **1** only; (*3–9*) **1** + CH_3SSCH_3, CH_3SSSCH_3, CO, triethylamine, propanoic acid, 4-ethylphenol, and CH_4, respectively. λ_{ex} = 365 nm.

Specificity of 1 toward CH_3SCH_3

The close resemblance of the UV-Vis and luminescent properties of the **1**-CH_3SCH_3-mixture to those of Re(*biq*)$(CO)_3$(CN) suggest that the cyanide bridge between Re(I) and Pt(II) of the dinuclear complex is cleaved after binding of the CH_3SCH_3 molecules to the Pt(II) center. This is supported by the observation of $\{[Re(biq)(CO)_3(CN)]\bullet Na\}^+$ (*m/z* 575.7 $[M + Na]^+$) and $[Pt(CH_3SCH_3)(DMSO)Cl]^+$ (*m/z* 371.0) in the electrospray ionization mass spectrum of the **1**-CH_3SCH_3-mixture. The substrate selectivity of the binding-induced dissociation is likely attributable to the preferential coordination of the sulfide functionality to Pt(II). Figure 3 shows the proposed recognition and signaling mechanism of complex **1** toward CH_3SCH_3.

Analyte Selectivity

Stability of chemodosimetric BmDAEs is an important factor affecting their analyte-specificity in competitive displacement assays. If the interaction between the molecular receptor and signaling unit is insufficient, the resultant ensemble cannot achieve good analyte specificity because the analytes may not be

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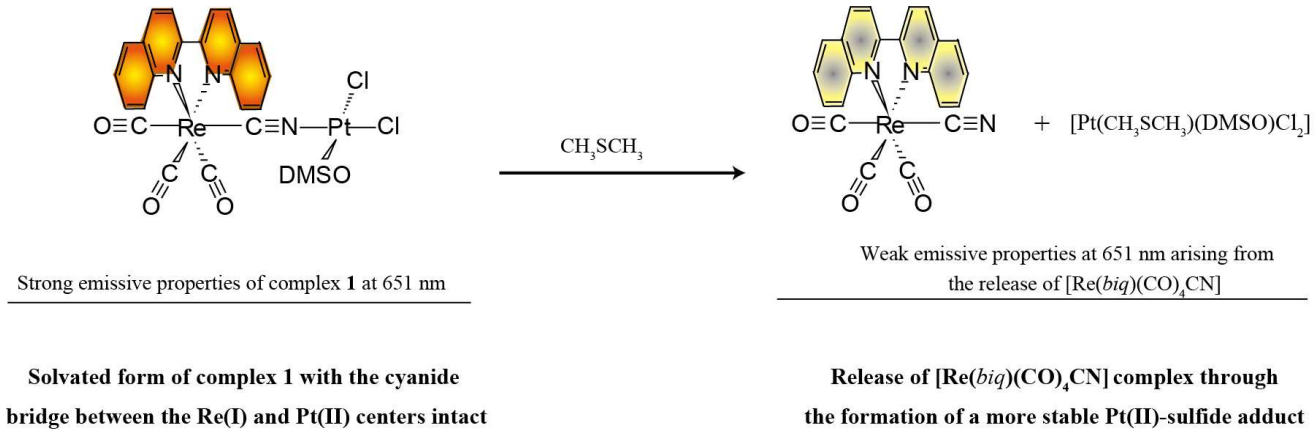

Figure 3. Proposed molecular recognition and luminescence signaling mechanism of complex **1** toward CH_3SCH_3.

able to out-compete the signaling unit to bind with the receptor. On the other hand, if the interaction is too strong, the complex may not be responsive to any analyte at all. In this context, competitive displacement of the indicator by biogenic sulfide in the presence of heterobimetallic donor–acceptor chemodosimetric systems can be viewed as occurring because of the following two equilibria:

$$\Delta G_A^\circ = Re(Lig)(CO)_3(CN) + Pt(DMSO)_2Cl_2 \rightarrow [Re(Lig)(CO)_3(CN)]\text{–}[Pt(DMSO)(Cl)_2] + DMSO \quad (1)$$

$$\Delta G_B^\circ = Pt(DMSO)_2Cl_2 + Analyte \rightarrow [Pt(Analyte)\ (DMSO)(Cl)_2] + DMSO \quad (2)$$

where $\Delta G_A°$ and $\Delta G_B°$ are the free-energy changes of the forward reactions 1 and 2, respectively. In order to understand how the stability of the ensembles and acceptor metal-analyte adducts affects the analyte selectivity of complex **1**, (i) two similar Re(I)-Pt(II) bimetallic complexes, [Re(*5-ph-phen*)$(CO)_3$(CN)]–[Pt(DMSO)$(Cl)_2$] **(2)** and [Re(*bpy*)$(CO)_3$(CN)]–[Pt(DMSO)$(Cl)_2$] **(3)** were synthesized, and (ii) the behavior of all ensembles (**1 – 3**) with different $\Delta G_A°$ and $\Delta G_B°$ were compared in detail. Figure 4a (Table S5) shows a comparison of the energy of formation ($\Delta G°$) of the formation of adducts between $Pt(DMSO)_2Cl_2$ and the BVCs, Re(*biq*)$(CO)_3$(CN), Re(*5-ph-phen*)$(CO)_3$(CN), and Re(*bpy*)$(CO)_3$(CN). The $\Delta G°$ values of ensembles **1**, **2**, and **3** are −21.5, −22.7, and −22.9 kJ mol^{-1} respectively and follow the order **3** > **2** > **1**. (Fig. S14-16)

More importantly, the $\Delta G_A°$ values of complexes **2** and **3** are much smaller than those for the formation of all Pt(II)–analyte adducts, while the $\Delta G_A°$ of complex **1** is smaller than those for the formation of most Pt(II)–analyte adducts, except for that with dimethyl sulfide. From the responses of these donor–acceptor ensembles, it is evident that successful competitive displacement of the luminescent donors can only occur when the energy of formation of the donor–acceptor chemodosimetric ensemble is higher than that of the resultant Pt(II)–analyte adduct (i.e., $\Delta G_A° > \Delta G_B°$; when more stable Pt(II)–analyte adducts could be formed). Figures 4c–e show the luminescent responses of "stronger" ensembles **2** and **3** toward the BVCs. Because their energy of formations are smaller than those of all Pt(II)–analyte adducts, the ensembles were not responsive to any of the BVCs. Figure 4b shows the luminescent responses of the suitable ensemble, i.e., **1**, toward the BVCs. As the formation energy of **1** is smaller than those of all the Pt(II)–analyte adducts except Pt(II)–CH_3SCH_3, it responded only to CH_3SCH_3. The results obtained from these Re(I)-based donor–acceptor ensembles illustrate the effect of the relative stability of the ensembles on their analyte selectivity. It also suggests that the analyte selectivity may be tuned by choosing different metal–ligand combinations in the signaling metal complex, which is in contrast to our previous experience of choosing different metallic acceptor–metallic donor combinations.[9b]

Detection of Gaseous Dimethyl Sulfide in Swine Sample by Complex 1

For final verification of the chemodosimetric concept, complex **1** was used to examine the freshness of a swine loin sample from a domestic pig (*Sus scrofa domesticus*). The spectrofluorimetric responses of complex **1** toward spiked dimethyl sulfide (0 to 150 ppm) in homogenized swine loin samples showed a linear

spectrofluorimetric response (R = 0.99) with respect to the dimethyl sulfide concentration (Fig. S17). By plotting the best-fit

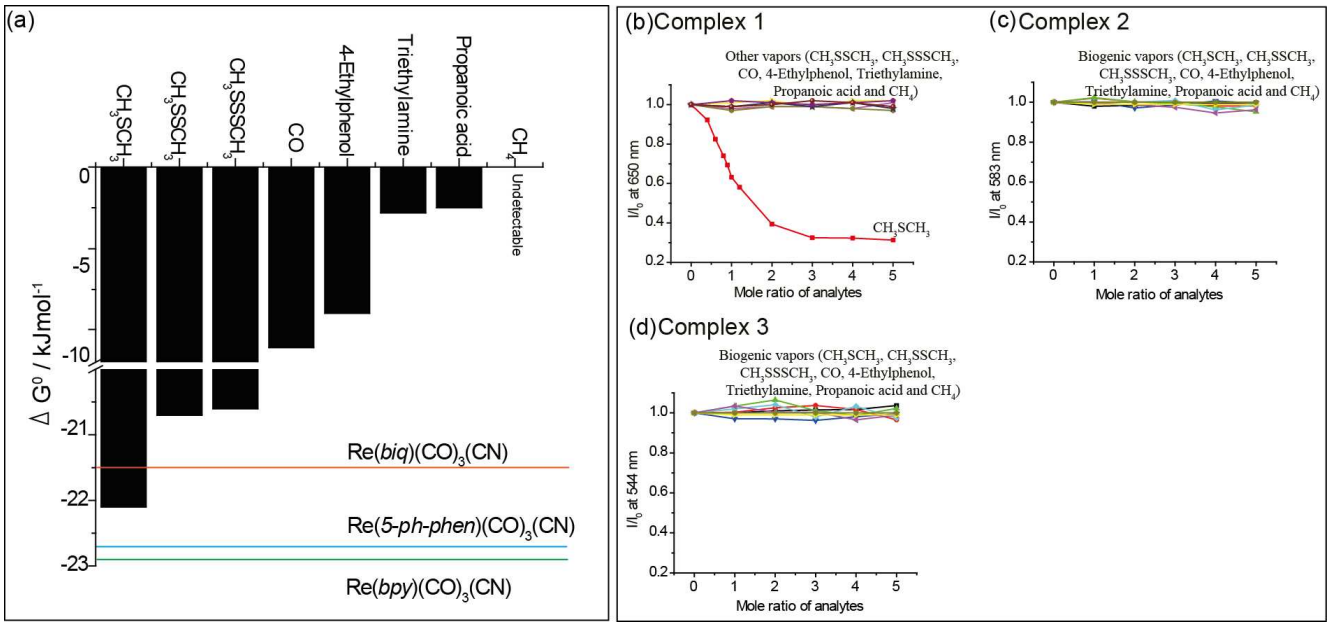

Figure 4. Spectrofluorimetric responses of complexes **1**–**3** toward BVCs. (a) Bar chart showing binding strength ($\Delta G_B°$) of Pt(II)(DMSO)Cl_2–analyte adducts. Horizontal lines on bar chart represent binding strength ($\Delta G_A°$) of complexes **1**–**3**. (b–e) Results of spectrofluorometric titration (I/I_0) of complexes **1**–**3** (1.0×10^{-4} M), respectively, with various BVCs as a function of their concentration. All titrations were carried out in 1.0×10^{-4} M $CHCl_3$ solutions of the complex at 298 K

of the graph of I/I_0 versus [spiked dimethyl sulfide], the slope and *y*-intercept were calculated to be 1.59×10^{-3} and 1, respectively. The spectrofluorimetric responses of complex **1** toward a mixture of dimethyl sulfide and BVCs were similar to those toward dimethyl sulfide alone (inset of Fig. S17, sets 1 and 2). However, there was no change in the spectrofluorimetry of complex **1** when spiking with either a mixture of the other BVCs or each of the vapors (inset of Fig. S17, sets 3–10). These results show that the other BVCs do not interfere with the luminescent response of **1** toward dimethyl sulfide.

Figure 5 summarizes the results of the spectrofluorimetric titrations of **1** (1×10^{-4} M) with the headspace vapor from swine, cattle, and poultry samples stored at 30 and 4 °C. Complex **1** shows a linear spectrofluorimetric response with increased storage time for the meats stored at 30 °C. However, there was no observable spectrofluorimetric change in complex **1** with increasing storage time when the samples were stored frozen (4 °C). These results are as expected because exposure of meats to elevated temperatures for extended periods of time enables spoilage bacteria to grow and convert sulfur-containing amino acids into biogenic sulfides.[1] Lowering the temperature impairs the growth of these bacteria and the production of those biogenic sulfides. From the best-fitted graph of I/I_0 versus time for pork, beef, and chicken samples stored at room temperature, the slope and *y*-intercepts were determined to be -2.35×10^{-3} and 1.00 (R = 0.991), -8.40×10^{-4} and 1.00 (R = 0.997), and -5.77×10^{-4} and 1.00 (R = 0.992), respectively. The differences in these values may be due to the different amounts of sulfur-containing amino acids/biomolecules in the meats.

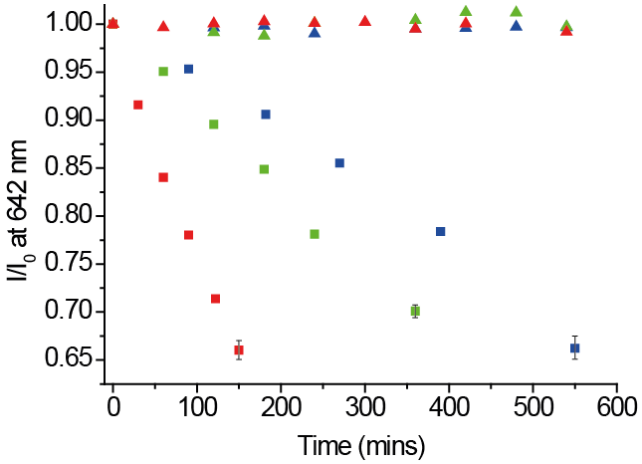

Figure 5. Spectrofluorometric titrations (I/I_0 at 650 nm) of complex **1** (1×10^{-4} M) to 75.0 g homogenized pork (red), chicken (green), and beef (blue) samples stored at (■) room temperature and (▲) 4 °C as a function of time. All titrations were performed in chloroform at 298 K. The best-fit line of the graph of I/I_0 versus time for (i) pork, (ii) beef, and (iii) chicken samples stored at room temperature revealed slopes and y-intercepts of (i) -2.35×10^{-3} and 1.00 (R = 0.991), (ii) -8.40×10^{-4} and 1.00 (R = 0.997), and (iii) -5.77×10^{-4} and 1.00 (R = 0.992), respectively. The data points were the mean value of three independent runs (with error bar showing ± 1 S.D.).

Conclusions

A heterobimetallic Re(I)-Pt(II) complex, [Re(*biq*)$(CO)_3(CN)$]–[Pt(DMSO)$(Cl)_2$] **(1)**, was synthesized and characterized. Its photophysical properties were reported, in addition to the crystallographic data for complex **1**. Complex **1** was found to be a luminescent chemodosimeter that is selective for biogenic sulfide vapors (dimethyl sulfide) with a detection limit down to 0.96 ppm. The analyte selectivity of this bimetallic chemodosimeter was studied with respect to the relative stability of the Pt(II) metal center between the Re(I) metal center and analytes, which was controlled by the Re(I)-ligand combination. Complex **1** can be used as a chemodosimeter to detect the freshness of beef, chicken, and pork samples.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [X-ray crystallographic data, 1H-NMR, ES-MS spectra, synthetic procedures and spectroscopic/spectrofluorimetric analyses are described in detail in the Supporting information.]. See DOI: 10.1039/b000000x/

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10 X-ray characterization results, synthetic procedures and spectroscopic/spectrofluorimetric analyses are described in detail in the Supporting information.

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