Development of sensitive and selective food sensors using new Re(I)-Pt(II) bimetallic complexes to detect volatile biogenic sulfides formed by meat spoilage

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ABSTRACT

Detection of volatile biogenic sulfides (VBS) plays a crucial role in food safety because the amounts of these compounds can reflect the freshness of meat. A new indicator-displacement assay with Re(I)-Pt(II) complexes, $[Re(Lig)(CO)_3(bridge)]$–$[Pt(DMSO)(Cl)_2]$ (**1**: Lig = 5-phenyl-1,10-phenanthroline and $bridge$ = NCS^-; **2**: Lig = 5-phenyl-1,10-phenanthroline and $bridge$ = CN^-; **3**: Lig = 2,2′-biquinoline and $bridge$ = NCS^-), was demonstrated to be a very effective sensing method to VBS. The results indicated that the control of Re(I)–bridge–Pt(II) and Re(I)–ligand combination are able to regulate their sensing selectivity and sensitivity. This system was successfully applied to detect CH_3SCH_3 in real rotten pork with a linear luminometric response up to 20.0 mg kg^{-1} (R = 0.997) with the detection limit as 0.05 mg kg^{-1}. Complex **1** also gave comparable results on the detection of VBS with respect to those determined by GCMS with recovery range from 76% to 102% (RSD% = 13.8).

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1. Introduction

The development of new methodology to control the performance of contaminant detection, such as the selectivity and sensitivity, through the use of indicator-displacement assay (IDA) techniques is extremely important (Moragues, Martinez-Manez, & Sancenon, 2011; Norouzy, Azizi, & Nau, 2015; Nguyen & Anslyn, 2006; Amendola, Bergamaschi, Buttafava, Fabbrizzi, & Monzani, 2010). Sensing technology is of great significance in our daily life. Food safety and quality are always a big public concern and reliable monitoring systems or sensors are crucial to maintain various foods, particularly meats, are stored properly and are not

rotten before consumed. A common practice on monitoring the freshness of meats is to check some biomarkers such as volatile biogenic sulfides (VBS), amines, carboxylic acids, and phenol released from rotten meats (Alexandrakis, Brunton, Downey, & Scannell, 2012; Mikš-Krajnik, Yoon, & Yuk, 2015; Lovestead & Bruno, 2010; Tománková, Bořilová, Streinhauserová, & Gallas, 2012; Varlet & Fernandez, 2010; Al-Attabi, D'arcy, & Deeth, 2009; Isogal et al., 2009; Romano, Perello, deRevel, & Lonvaud-Funel, 2008). VBS is a typical class of low molecular weight thiol-containing compounds including RSR, RSSR, and RSSSR (R = alkyl- or H) to. For example, the spoilage of meat products results in the generation of rancid and putrid odors, which usually contain hydrogen sulfide (H_2S), methanethiol (CH_3SH), dimethyl disulfide (CH_3SSCH_3), dimethyl trisulfide (CH_3SSSCH_3), and especially dimethyl sulfide (CH_3SCH_3) that is one of the most abundant VBS found in rotten meats (Lovestead & Bruno, 2010; Varlet & Fernandez, 2010; Isogal et al., 2009; Mayr et al., 2003). However, all these biomarkers are usually weaker nucleophiles than charged species. In addition to their low concentrations (from µg kg^{-1} to mg kg^{-1}) in the headspace over meat, there are also many

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surrounding interfering fragrances. Therefore, molecular probes that can instantaneously, selectively, and sensitively detect VBS are highly desirable. Instrumental methods such as chromatography and electrophoresis are the most conventional practices used for their detection currently (Azad, Ohira, & Toda, 2006; Mayr et al., 2003; McDermott, Terry, Conlan, Barnett, & Francis, 2011; Nagahata, Kajiwara, Ohira, & Toda, 2013; Shirasu, Nagai, Hayashi, Ochiai, & Touhara, 2009; Vasta, Ratel, & Engel, 2007; Watanabe, Ueda, Higuchi, & Shiba, 2008). However, these *ex-situ* methods can only identify spoilage problems after the rotten food has been consumed. In recent years, some advanced methods for on-site and instant analysis of trace sulfide have also been reported using chemiluminescence (Azad et al., 2006; McDermott et al., 2011; Nagahata et al., 2013). From the point of view of real-time detection and rapid screening, the use of a bimetallic-based IDA technique would be a better approach, because it can be designed for a specific purpose, such as tuning its selectivity and sensitivity through the use of combination of two metal centers, coordinating ligands, and bridging molecules. Sensors development with this tactic is rarely found in literature.

We have previously worked on a number of cyano-bridged bimetallic donor-acceptor ensembles (BmDAEs), M_D—C≡N—M_A, as chemodosimeters for sensing and detection of various biological and environmental analytes (Chow, Gong, & Gong, 2014; Chow, Ho, & Gong, 2015; Chow, Lam, & Wong, 2005; Chow, Lam, & Wong, 2013). We find that the design of the BmDAEs are very suitable for detecting volatile thiol-containing compounds from rotten foods particularly for meats because the chemodosimetric reaction is irreversible, thus the spoilage indicator signal cannot be reversed, and thus customers are able to identify clearly whether contamination occurred (Chow et al., 2013; Chow et al., 2014). Our recent results of a Re(I)—C≡N—Pt(II) bimetallic system indicated that the luminescent chemodosimetric selectivity for VBS could be tuned by choosing different Re(I)–ligand combinations. We found that the sensitivity of that system in the presence of a variety of interfering vapors could be reached with a detection limit as low as 0.96 mg kg^{-1} with the binding constant (log $K_{overall}$) toward dimethyl sulfide as 3.63 ± 0.03 (Chow et al., 2014). We postulate that, not only the metal–ligand combination of a bimetallic system determines the selectivity and sensitivity of the system, its metal–bridge as well as metal–ligand combination also affect these two outcomes of the system. Therefore, in contrast to our previous studies of choosing only different metal–metal (Chow et al., 2005), metal–bridge (Chow et al., 2015), or metal–ligand combinations (Chow et al., 2014), in this study we intensively investigated the sensing performance of a Re(I)–Pt(II) bimetallic system through the regulation of both of its bridging and chromotropic ligands. To demonstrate the usefulness of the bimetallic-based IDA technique in the quality control of meat, we herein report an ultra-sensitive and selective chemodosimeter, Re(5-*ph-phen*)(CO)$_3$(N=C=S)]–[Pt(DMSO)(Cl)$_2$] (**1**: 5-*ph-phen* = 5-phenyl-1,10-phenanthroline), for the detection of VBS in real pork samples. The controlled selectivity and sensitivity of complex **1** involved the rational selection of (i) bridging and (ii) organic ligands in the bimetallic [Re(*Lig*)(CO)$_3$(*bridge*)]–[Pt(DMSO)(Cl)$_2$] systems. To verify the chemodosimetric concept, complex **1** was used to examine the concentration of CH$_3$SCH$_3$ and CH$_3$SH which occur most abundantly during improper storage of food (Mayr et al., 2003), in real pork samples. In this study, a naked-eye luminometric response was generated remarkably with a linear luminometric response (R = 0.997) toward CH$_3$SCH$_3$ in a concentration range up to 20.0 mg kg^{-1} in the pork samples at 298 K. The analytical method was validated with a good recovery and RSD of 98.0% and 2.2%, respectively. The method detection limit (MDL) toward CH$_3$SCH$_3$ in real pork samples by complex **1** was found as 0.05 mg kg^{-1}. The analytic results obtained towards the

detection of CH$_3$SH by complex **1** were comparable to those determined by GCMS with recovery range from 76% to 102% (RSD% = 13.8). To our best knowledge, complex **1** is the most sensitive chemodosimeter for the detection of dimethyl sulfide. (Despite the amount of literature regarding the detection of thiol-compounds (RSH), there are few molecular probes for RSR) (Chen, Zhou, Peng, & Yoon, 2010; Fu, Li, Hu, & Zhu, 2005; Ros-Lis et al., 2004; Wang, Han, Jia, Zhou, & Deng, 2012; Qian & Lin, 2014). Its analog complex **2** and **3** were also synthesized to illustrate the effects of the bridging and chromophore ligands on the selectivity and sensitivity in the sensing system.

2. Experimental section

2.1. Materials and general procedures

The ligands (*Lig*), 2,2′-biquinoline (*biq*) and 5-phenyl-1,10-phenanthroline (5-*Ph-phen*); and KSCN, dimethyl sulfide (99%) and sodium thiomethoxide (95%) were obtained from Aldrich (St. Louis, MO, USA). Dimethyl disulfide (99%) was obtained from Acros (Geel, Belgium). Dimethyl trisulfide (98%) was purchased from TCI (Toyko, Japan). Other chemicals were obtained according to the literature (Chow et al., 2014). Re(*Lig*)(CO)$_3$Cl, Re(*Lig*)(CO)$_3$(CN), Re(*Lig*)(CO)$_3$(NCS), and Pt(DMSO)$_2$Cl$_2$ were prepared following to literature (Leasure et al., 1991; Pfennig, Chen, & Meyer, 1996; Price, Williamson, Schramm, & Wayland, 1972; Takeda, Koike, Inoue, & Ishitani, 2008). The common organic solvents used in syntheses and spectroscopic titrations were analytical grade. Complexes **2** and **3** were synthesized and reported in Supporting Information (SI.).

2.2. Synthesis and characterization

2.2.1. Re(5-ph-phen)(CO)₃(NCS)

The Re-complex was synthesized using a modification of the method reported for Re(*bpy*)(CO)$_3$(NCS) by Takeda (Takeda et al., 2008): An 80% ethanol (150 mL) containing Re(5-*ph-phen*)(CO)$_3$Cl (0.281 g, 0.500 mmol) and KSCN (2.400 g, 0.025 mol) was refluxed under a N$_2$ atmosphere for 12 h. Over the course of the reaction, the reaction mixture became a suspension of a yellow precipitate, which was then cooled. The crude product was collected and washed several times with 30 mL of deionized water, 30 mL of ethanol, and then 30 mL of diethyl ether. An air-stable yellow solid product was isolated (88% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.39 (s, 2H), 8.62 (d, J = 5.0 Hz, 2H), 8.02 (s, 1H), 7.96 (m, 1H), 7.87 (m, 1H), 7.59 (m, 3H), 7.52 (m, 2H). IR (KBr disc): $v_{C≡N}$ = 2093 cm^{-1}; $v_{C≡O}$ = 2019, 1936, and 1909 (br) cm^{-1}. ESI-MS (positive mode): m/z = 607.6 {[Re(5-*ph-phen*)(CO)$_3$(NCS)]·Na}$^+$. Anal. Calcd. for C$_{22}$H$_{12}$N$_3$O$_3$ReS: C, 45.20; H, 2.07; N, 7.19%. Found: C, 45.19; H, 2.11; N, 7.20%.

2.2.2. [Re(5-ph-phen)(CO)₃(NCS)]–[Pt(DMSO)(Cl)₂] (1)

Complex **1** was prepared by stirring Pt(DMSO)$_2$Cl$_2$ (0.0844 g, 0.2 mmol) with one equivalent of Re(5-*ph-phen*)(CO)$_3$(NCS) (0.1169 g, 0.2 mmol) in a methanol/chloroform mixture (1:1, 100 mL) at ambient condition for 30 min. The solution was concentrated to dryness *in vacuo* and the crude product obtained was washed several times with cold MeOH and diethyl ether. An air-stable yellow solid product was isolated in good yield (98%). ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm = 9.33 (s, 2H), 8.62 (d, J = 10.0 Hz, 2H), 8.00–7.92 (m, 2H), 7.88–7.84 (m, 1H), 7.57 (m, 5H), 3.28 (s, 6H). IR (KBr disc): $v_{C≡N}$ = 2151 cm^{-1}; $v_{C≡O}$ = 2029 and 1905 cm^{-1}. ESI-MS (positive mode): m/z = 951.7 {[Re(5-*ph-phen*)(CO)$_3$(NCS)]–[Pt(DMSO)Cl$_2$]·Na}$^+$. Anal. Calcd. for C$_{24}$H$_{18}$Cl$_2$N$_3$O$_4$PtReS$_2$: C, 31.04; H, 1.95; N, 4.52%. Found: C, 31.10; H, 1.89; N, 4.48%.