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Heterobimetallic Ru(II)−Eu(III) Complex as Chemodosimeter for Selective Biogenic Amine Odorants Detection in Fish Sample

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Gaseous biogenic amines such as putrescine, spermidine, aniline, and trimethylamine are important biomolecules that play many crucial roles in metabolism and medical diagnostics. A chemodosimetric detection assay has been developed for those gaseous amines by Ru^{II}−Eu^{III} heterobimetallic complexes, $K\{[Ru^{II}(^{t}Bubpy)(CN)_4]_2Eu^{III}(H_2O)_4\}$ (where ^{t}Bubpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine). Synthesis, X-ray crystal characterization, and spectroscopic properties of this Ru^{II}−Eu^{III} heterobimetallic complex were reported. Binding properties of the Ru^{II}−Eu^{III} complex with common gases revealed that this complex is very selective to gaseous amine molecules. Sensitivity of this complex toward the amines was found as ∼log k = 4.5−4.8. Real time monitoring of gaseous biogenic amines was applied to real fish samples (Atlantic mackerel) by studying the spectrofluorimetric responses of the Ru^{II}−Eu^{III} complex toward different biogenic amine concentration. GC/MS studies were also used as a reference for the studies. A linear spectrofluorimetric response was found toward biogenic amine concentration in real fish samples. This complex was found to respond specifically to those biogenic amines down to 10 ppb.

The detection of biologically important analytes, especially neutral molecules, through supramolecular sensors and dosimeters is a demanding task. Neutral biogenic amines are of particular interest due to their impact in areas ranging from biomarkers of diseases[1] to quality control of foodstuffs.[2] Biogenic amines such as histamine, spermidine, and putrescine are the key compounds in living systems and are involved in many vital biological functions such as protein synthesis, regulation of cell proliferation, and modulation of gene expression.[3] Medical and pharmaceutical research has focused on these amines in order to clarify the mechanisms for some of the biological disorders. For instance, a high plasma level of putrescine and spermidine is associated with breast, colon, and skin cancers.[1c−g] Histamine, which has been identified as a neurotransmitter for anthropod photoreceptors,[1j,k] is the causative agent of scombroid food poisoning. With the aim to open possibilities of pharmacological treatment in the disordered systems, effective methods to monitor these amino-biomarkers have been demanded. On the issues of food industry, a wide range of biogenic amines are found as biomarkers of spoiled fishes.[2e−h] Researchers have shown how biogenic amines, such as histamine, increase as seafood begins to spoil. Food scientists of all stripes should be interested in coming up with molecular probes in the hope of reducing a million cases of food poisoning each year in the world.

Chemodosimeters are molecular devices that interact with their analytes and yield physically measurable signals in an irreversible fashion. In contrast to ordinary chemosensors which respond to the real-time concentration of their analytes, chemodosimeters respond to their analytes in a cumulative manner.[4] This property allows chemodosimeters to be especially suitable for food monitoring. Since the signals do not disappear (irreversible fashion), users/customers can recognize if there is spoilage of food if contamination has occurred at any time during the process (for example, food production, transportation, or storage).

Methods of detecting biogenic amines recently described in the literatures have taken advantage of analytical instruments,[5] molecular imprinting polymers,[6] enzymes,[7] antibodies,[8] and array sensors.[9] However, scarce examples of supramolecular based

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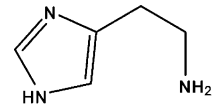
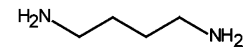
dosimeters can be found for the biogenic amines.[10] Rapidly detecting these amines in their vapor form and reporting the signal in a naked-eyed manner are particularly important. Our group has focused on the feasibility of using M_A—C≡N—M_B heterobimetallic coordination complexes as chemodosimetric compounds (M_A = Fe^{II}, Ru^{II}, and Os^{II}; M_B = Pt^{II}, Cu^{II}, and Ni^{II}) for the detection of various analytes.[11] With suitable metal ion combinations, it is envisioned that chemodosimeters with fine-tuned analyte specificity can be obtained.

Supramolecular assemblies are impacting the development of molecular materials,[12] particularly, chemosensing and chemodosimetric materials.[13] Of particular interest are those heterometallic assemblies as their intrinsic properties can be tuned by judicious choice of different metal and ligand combinations.[14] Heterobimetallic M_A—C≡N—M_B chemodosimeters based on the indicator displacement approach especially draw our attention. The indicator displacement approach resembles antibody-based immunoassays in that target analytes have to compete for specific molecular receptors with fluorogenic/chromogenic signaling analogs.[13a,b,15] As these heterobimetallic dosimetric materials contain a "metallic reporter" and a "metallic receptor" through a cyanide bridge, suitable reporters/receptors can be chosen, cases-to-cases, for the desired substrate/environment. Recently, Faulkner and Ward extensively studied the photophysical properties of lanthanide based heterobimetallic M_A—C≡N—M_B coordination complexes (M_A = Ru(II) complex; M_B = Ln(III) complex),[16] and several groups have taken advantage of energy transferring properties of heterobimetallic M_A—C≡N—M_B coordination complexes.[17] On the contrary, the use of heterobimetallic M_A—C≡N—M_B coordination complexes in the construction of chemodosimeters remains unexplored.

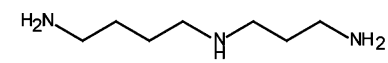
We are interested in the development of chemodosimeters that are capable of recognizing gaseous biogenic amines and can communicate the recognition event through a visual signal. In this work, the synthesis and characterization of a new Ru(II)—Eu(III) heterobimetallic donor—acceptor molecular chemodosimetric compound, $K\{[Eu(H_2O)_4][Ru(^tBubpy)(CN)_4]_2\}$ (**Ru_2Eu-1**) (^{t}Bubpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine), were reported. The compound was found to produce naked-eyed luminescent responses specifically to biogenic amines down to 10 ppb.



Histamine



Putrescine



Spermidine

EXPERIMENTAL SECTION

Materials and General Procedures. 4,4′-Di-*tert*-butyl-2,2′-bipyridine (^{t}Bubpy), potassium cyanide, $RuCl_3 \cdot 3H_2O$, $EuCl_3 \cdot 6H_2O$, aniline, histamine, putrescine, spermidine, and anhydrous gaseous NH_3 (99.99%) were obtained from Aldrich. Gaseous H_2S (99.5%) and CO (99.95%) were obtained from Hong Kong Special Gas Company. Gaseous CH_4 (99.95%), H_2 (99.995%), and N_2 (99.995%) were purchased from Hong Kong

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Oxygen Company. $K_2[Ru(^tBubpy)(CN)_4]$ was synthesized according to the literature method.[18] All solvents used were of analytical grade.

Physical Measurements and Instrumentation. Infrared spectra in the range 500−4000 cm^{-1} in KBr plates were recorded on a Perkin-Elmer Model FTIR-1600 spectrometer. UV−vis spectra were measured on a Hewlett-Packard 8452A ultraviolet visible diode array spectrophotometer. Emission spectra were recorded using a Horiba FluoroMax-3 spectrofluorimetric with 5 nm slit width and 0.5 s integration time. Electrospray mass spectra (ESI-MS) were measured by a PE SCIEX API 365 LC/MS/MS system. Elementary analyses were performed on a Vario EL elementary analyzer.

$K\{[Eu(H_2O)_4][Ru(^tBubpy)(CN)_4]_2\}\cdot 8H_2O$ (Ru_2Eu-1). A mixture of $K_2[Ru(^tBubpy)(CN)_4]$ (0.110 g, 0.2 mmol) and $EuCl_3\cdot 6H_2O$ (0.037 g, 0.1 mmol) was stirred in 5 mL of a water/methanol mixture (1:1) at room temperature for 30 min and was allowed to stand overnight. Yellow crystalline plates were obtained by slow evaporation of solvent. Yield: 0.084 g (69%). IR (KBr): $\nu_{C\equiv N}$ = 2061, 2105 cm^{-1}. ESI-MS (-ve mode): m/z 1099 $\{[Eu][Ru(^tBubpy)(CN)_4]_2\}^-$. Anal. Calcd for $C_{44}EuH_{56}KN_{12}O_4Ru_2\cdot 7H_2O$: C, 39.55; H, 5.28; N, 12.58. Found: C, 39.54; H, 5.24; N, 12.58.

Crystal Structure Determination. Yellow single plated crystals of complex **Ru_2Eu-1** were grown by slow evaporation of its corresponding aqueous methanol solution in open atmosphere. Geometric and intensity data for the complex was collected on a Bruker SMART 1K CCD area detector with graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). The crystal of the complex used for data collection was mounted in glass capillaries to prevent rapid solvent loss. The collected frame was processed with the software CrystalClear (Rigaku).[19] The data was corrected for Lorentz and polarization effects. A correction for secondary extinction[20] was applied to the collected reflections. The structure of the complex was solved by direct methods (SHELX97[21]) in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyzed on F^2. Non-hydrogen atoms were refined with anisotropic displacement parameters except for the atoms of some of the free water molecules where these atoms were refined isotropically. The hydrogen atoms were generated in their idealized positions and allowed to ride on the respective carbon atoms. Crystal data and experimental details are summarized in Supporting Information (SI) Tables 1 and 2.

UV−Vis Spectroscopic and Spectrofluorimetric Titrations. All solvents used in UV−vis spectroscopic and spectrofluorimetric titrations were of analytical grade. All the titrations were carried out in ethanol. Measurements were taken after equilibrium had been reached between the receptor and substrate. A 1:1 receptor−substrate interaction was analyzed according to Benesi−Hildebrand equations[22] for UV−vis spectroscopic titration (eq i) or spectrofluorimetric titration (eq 2), while 1:2 receptor−substrate interaction was determined by either UV−vis spectroscopic titration (eq 3) or spectrofluorimetric titration (eq 4).

Formation constants (log K's) were estimated from the ratio of the y-intercept and the slope of straight lines obtained by plotting $A_0/(A - A_0)$ or $I_0/(I - I_0)$ versus $[M]^{-1}$ or $[M]^{-2}$ depending on 1:1 or 1:2 receptor−substrate interaction, respectively.

$$\frac{A_0}{A - A_0} = \left(\frac{\varepsilon_0}{\varepsilon_0 - \varepsilon}\right)\left(\frac{1}{K_B[\text{substrate}]} + 1\right) \quad \text{(i)}$$

$$\frac{I_0}{I - I_0} = \left(\frac{a}{b - a}\right)\left(\frac{1}{K_B[\text{substrate}]} + 1\right) \quad \text{(ii)}$$

$$\frac{A_0}{A - A_0} = \left(\frac{\varepsilon_0}{\varepsilon_0 - \varepsilon}\right)^2\left(\frac{1}{K_B[\text{substrate}]^2} + 1\right) \quad \text{(iii)}$$

$$\frac{I_0}{I - I_0} = \left(\frac{c}{d - c}\right)^2\left(\frac{1}{K_B[\text{substrate}]^2} + 1\right) \quad \text{(iv)}$$

$$\text{detection limit} = t \times s.d. \quad \text{(v)}$$

A_0 and A are the absorbances of the chromogenic reagent in the absence and presence of the substrate; ε_0 and ε are the corresponding molar absorption coefficients of the chromogenic reagent in the absence and presence of the substrate. I_0 and I are luminescence intensities of the fluorogenic reagent in the absence and presence of the substrate; a, b, c, and d are constants; [substrate] is the concentration of target analyte. t is the compensation factor from *Student's t Distribution Table*, and *s.d.* is the standard deviation of the relative luminescence intensity.

Mole Ratio of Ru(II)−Eu(III) Donor−Acceptor Compound in Ethanol: Mole Ratio Plot. A series of acceptor (i.e., $EuCl_3\cdot 6H_2O$) solutions (0 to 6.7×10^{-4} M) were mixed with the donor (i.e., $K_2Ru(^tBubpy)(CN)_4$) solutions (3.3×10^{-4} M). Spectral changes at 651 nm (I/I_0) of the resulting mixtures were plotted as a function of mole fraction of the acceptor. The sharp turning point from the mole ratio plot revealed the mole ratio between donor and acceptor compounds in ethanol [SI Figure 2].

Formation Constants of Ru_2Eu-1−Biogenic Amine Adducts. UV−vis spectroscopic and spectrofluorimetric titrations of solutions of **Ru_2Eu-1** (3.33×10^{-5} M) by biogenic amine solutions putrescine (0 to 6.67×10^{-5} M), histamine (0 to 6.67×10^{-5} M), spermidine (0 to 6.67×10^{-5} M), aniline (0 to 3.33×10^{-2} M), and ammonia (0 to 8.33×10^{-5} M) were carried out in ethanol. Observed absorbance at 440 nm and luminescent

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at 644 nm of the resultant mixtures were measured. Formation constants of the **Ru_2Eu-1**−analyte adducts were analyzed by fitting the titration curves with the 1:2 Benesi−Hildebrand equation (eq 4) (Table 2).

Mole Ratio of Ru_2Eu-1 toward Various Biogenic Amines in Solution: Mole Ratio Plot. A series of analytes (aniline, putrescine, histamine, spermidine, NH_3, and H_2S(g), CO(g), CH_4(g), H_2(g), N_2(g), and atmospheric air) (0 to 5×10^{-4} M) were mixed with **Ru_2Eu-1** solutions (1.0×10^{-4} M). Spectral changes at 640 nm (I/I_0) of the resulting mixtures were plotted as a function of mole fraction of the analyte. The sharp turning point from the mole ratio plot revealed the mole ratio between **Ru_2Eu-1** and analyte compound in ethanol (Figure 4).

Detection Limits of Chemodosimeter (Ru_2Eu-1) toward Various Biogenic Amines. A series of 10 ethanolic solutions of **Ru_2Eu-1** (3.3×10^{-5} M) were added with a fixed known concentration of analytes (aniline, putrescine, histamine, spermidine, NH_3, and H_2S(g), CO(g), CH_4(g), H_2(g), N_2(g), and atmospheric air). Spectroscopic changes of the resultant mixtures were recorded. The detection limits were calculated with eq 5. Table 2 summarized the detection limits of the **Ru_2Eu-1** with various analytes.

Luminometric Responses of Ru_2Eu-1 toward Various Vapors. Luminometric responses of the chemodosimeters toward various vapors were monitored by purging biogenic amine vapors and common vapors (1 atm, 3 mL) aniline(g), histamine(g), putrescine(g), spermidine(g), NH_3(g), H_2S(g), CO(g), CH_4(g), H_2(g), N_2(g), and atmospheric air into the headspace of the ethanolic solutions of **Ru_2Eu-1** (2.0×10^{-4} M) at 25 °C. The purging volume was 3 mL for all of these analytes. Except for histamine, aniline, putrescine, and spermidine, all the other analytes were already in gaseous form which can be injected directly into the headspace of the ethanolic solutions of the chemodosimeters. For aniline and putrescine they were first purified by distillation before being heated up in an enclosed flask to obtain their vapors. For histamine and spermidine, direct heating was applied on its solid in an enclosed flask in order to collect its vapor for analysis. The spectroscopic changes of the resultant mixtures in regular time intervals were recorded. After reaching its equilibrium (no spectral changes with respect to time anymore), the luminescent responses to the analytes were obtained by digital photography (Figure 5).

Detection of Gaseous Biogenic Amines in Fish Sample by Ru_2Eu-1. A 0.5 kg fresh Alantic mackerel (*Scomber scombrus*) loin was purchased from a local fish market. The meat was homogenized in a food processor. Immediately following the processing, a series of three samples of 20.0 g of homogenized meat were separately sealed in a 50 mL glass container. They were kept in different storing conditions, i.e., room temperature, frozen temperature (0 °C), and room temperature with 60 g of preservatives ($NaNO_2$). According to the storing time, 3.0 mL of gaseous vapor from the headspace of the fish filling container of each storing condition was taken and injected into three different ethanolic solutions of **Ru_2Eu-1**. After equilibrium (no spectral changes with respect to time anymore) was reached, luminescent responses (I/I_0) of **Ru_2Eu-1** were recorded as a function of time (Figure 7).

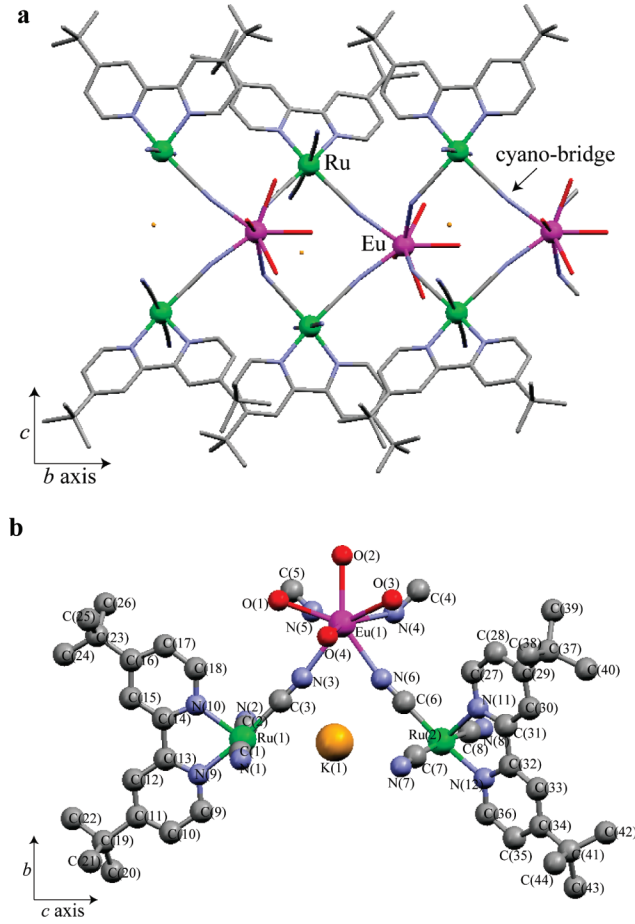

Figure 1. (a) Perspective views of part of the one-dimensional chain structure in **Ru_2Eu-1** along the *b* axis. (b) Perspective views of monomeric unit of **Ru_2Eu-1** with numbering scheme adopted. Hydrogen atoms and noncoordinated water molecules were omitted for clarity (Ru in green; Eu in purple; C in gray; O in red; N in blue; K in yellow).

RESULTS AND DISCUSSION

Synthesis and Characterization. The heterobimetallic complex **Ru_2Eu-1** was formed by simply stirring 2 equiv of $K_2[Ru(^tBubpy)(CN)_4]$ complex with 1 equiv of $EuCl_3 \cdot 6H_2O$ in a 1:1 volume ratio of a water/methanol mixture in open atmosphere at room temperature. The heterobimetallic complex was isolated as air-stable yellow platelike crystals in fairly good yield and were characterized by X-ray crystallography, ESI-MS, and microanalysis.

Ru_2Eu-1 is one-dimensional polymer chain with the corresponding $\{[Eu^{III}(H_2O)_4]\text{-}[Ru^{II}(^tBubpy)(CN)_4]_2\}^-$ monomeric units. Figure 1 shows the perspective views of the crystal structure of **Ru_2Eu-1**. One-dimensional linear polymer chains are formed along the *b*-axis of **Ru_2Eu-1** (Figure 1a). The coordination geometry of the Eu(III) centers is a distorted bicapped square pyramidal composed of four H_2O molecules and four cyanides. Each Eu(III) center is bridged to four Ru(II) centers via cyanide bridges. The monomeric unit of **Ru_2Eu-1** is shown in Figure 1b; there are two crystallographically independent $[Ru^{II}(^tBubpy)(CN)_4]^{2-}$ units and one Eu(III) center which form a v-shape configuration connected with two Ru−C≡N−Eu cyanide bridges. In the crystal structures, some of the cyanides are bridging ligands and some are nonbridging.

Table 1. Electrospray Mass Spectroscopic Studies of Ru_2Eu-1 in Ethanol and IR Spectroscopic Studies of the Cyano Stretching Frequency ($\nu_{C\equiv N}$) of $K_2[Ru(^tBubpy)(CN)_4]$ and Ru_2Eu-1

complex	$\nu_{C\equiv N}$ (cm^{-1})[a]	m/z[c]
$K_2[Ru(^tBubpy)(CN)_4]$	2042 (s)[b], 2057 (s)[b], 2073 (s)[b], 2096 (s)[b]	513
Ru_2Eu-1	2061 (s)[b], 2105 (s)[b]	1099

[a] IR studies were performed by KBr pellet. [b] (s) = strong peak. [c] All the ES-MS were performed in ethanol and studied with negative mode.

The average bond distance of the nonbridged cyanides in **Ru_2Eu-1** are in the range 1.14−1.16 Å, while those of the bridged cyanides are in the range 1.16−1.17 Å. Similar molecular configurations have already been described by Faulkner and Ward[16] in two analogous complexes which are two-dimensional sheet neutral $\{[Ru(bpy)(CN)_4]_3[Ln(H_2O)_4]_2\}$ complexes (where Ln = Nd and Gd) and discrete bent shape molecular $K\{[Ru(bpy)(CN)_4]_2[Ln(H_2O)_m]\}$ complexes (where Ln = Pr, Er, Yb; m = 7, 6, 6, respectively). Formation of the cyano-bridged bimetallic complex was also confirmed by IR spectroscopic studies where $\nu_{C\equiv N}$ bands of $K_2[Ru(^tBubpy)(CN)_4]$ at 2042, 2057, 2073, and 2096 cm^{-1} were changed to two new $\nu_{C\equiv N}$ bands, 2061 and 2105 cm^{-1}, after coordinating to Eu(III) (Table 1).

Characterizations of the solvated form of **Ru_2Eu-1** were performed in organic solvent. The complex is soluble in polar organic solvents such as ethanol, methanol, DMSO, and DMF. When the complex is dissolved in the polar solvents, it readily dissociated into its solvated monomeric units. Integrity of the cyanide bridges of the monomeric unit of complex **Ru_2Eu-1** in ethanol is demonstrated by its electrospray mass spectra showing peaks at m/z 1099 $\{[Eu][Ru(^tBubpy)(CN)_4]_2\}^-$ (Table 1 and SI Figure 1). Furthermore, spectrofluorometric titrations (mole ratio plot) of $K_2[Ru(^tBubpy)(CN)_4]$ with $EuCl_3 \cdot 6H_2O$ solution in ethanol show that the solvated form of **Ru_2Eu-1** is in a ratio of 1:2 (Eu(III):Ru(II)) (SI Figure 2).

Electronic Absorption and Luminescent Properties. Photophysical properties of the $K_2[Ru(^tBubpy)(CN)_4]$ donor unit are known to be strongly dependent on its environment.[23] With reference to previous spectroscopic works, interaction between the lone-pair electrons of the cyanide ligands and surrounding electron accepting ions/molecules affects the energy of the $Ru(d\pi) \rightarrow {}^tBubpy\ (\pi^*)$ MLCT absorption band as well as the ^{3}MLCT emission.[24] Figure 2 shows the comparison of the MLCT absorption as well as ^{3}MLCT emission between $K_2[Ru(^tBubpy)(CN)_4]$ and **Ru_2Eu-1**. The ethanolic solution of $K_2[Ru(^tBubpy)(CN)_4]$ is yellow in color with UV−vis absorption λ_{max} at 435 nm and gives a strong luminescence at λ_{max} 654 nm with a lifetime of 97 ns. Upon coordination to become complex **Ru_2Eu-1**, the MLCT absorption band of the Ru(II)−diimine chromophore blue-shifted from 435 to 417 nm and the ^{3}MLCT emission drastically quenched in luminescent intensity, accompanied by a similar lifetime of 106 ns. The concomitant blue-shift in both of the MLCT electronic transition and ^{3}MLCT

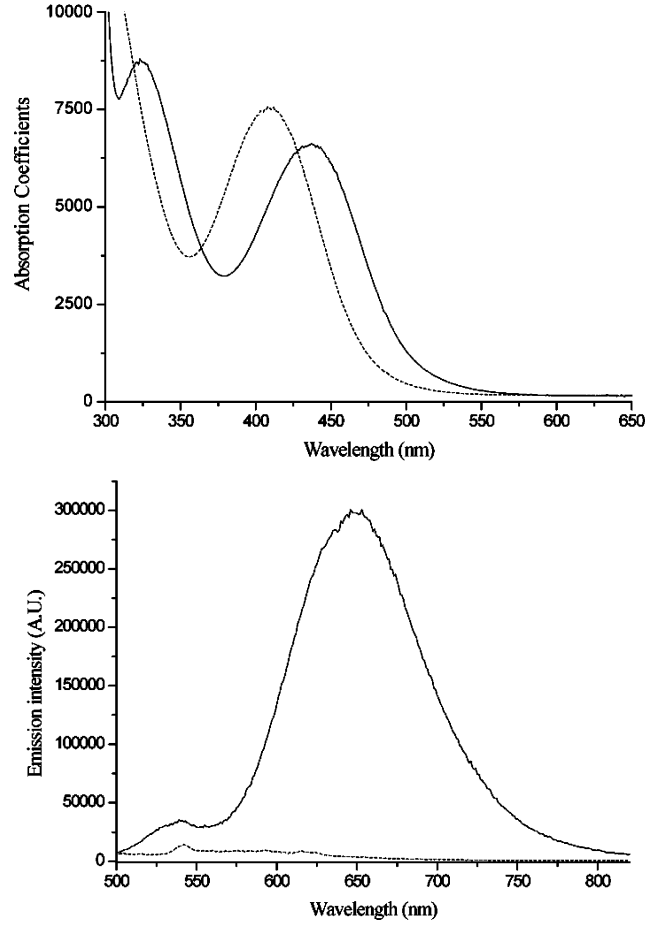

Figure 2. (top) Absorption spectra of $K_2[Ru(^tBubpy)(CN)_4]$ (—) and **Ru_2Eu-1** (---) in EtOH at 298 K.(bottom) Luminescence spectra of $K_2[Ru(^tBubpy)(CN)_4]$ (—) and **Ru_2Eu-1** (---) in EtOH at 298 K. The spectra were obtained with excitation at 466 nm with concentration 2 × 10^{-4} M.

emission in the Ru−Eu complexes is understandable in terms of the electron-withdrawing effect of the Eu(III) acceptor on stabilizing the d-orbitals of the Ru(II)−diimine chromophore. The effect is consistent with those observed in a number of related solventochromic systems in which protons,[23] boron halides,[25] and transition-metal ions[26] act as Lewis acids.

Binding Properties of Ru_2Eu-1 with Various Vapors. According to our previous studies[11] of heterobimetallic donor−acceptor coordination complexes, $M_A{-}C{\equiv}N{-}M_B$ (M_A = Fe^{II}, Ru^{II}, and Os^{II}; M_B = Pt^{II}, Cu^{II}, and Ni^{II}), it is envisioned that heterobimetallic complexes with different donor−acceptor combinations can produce specific sensing properties toward different kinds of analytes. In this case, Eu(III) acceptors are well-known hard Lewis acids which have a general strong affinity to hard bases such as nitrogen-containing molecules. Therefore, we tried to use **Ru_2Eu-1** complex to detect volatile biogenic amines. Figure 3 shows the UV−vis spectroscopic and spectrofluorometric titrations of **Ru_2Eu-1** to histamine. (SI Figures 3−6 show the titrations of **Ru_2Eu-1** toward other biogenic amines including putrescine, spermidine, aniline, and ammonia.) Upon addition of histamine to the ethanolic solutions of **Ru_2Eu-1**, the MLCT transitions of the complex were shifted

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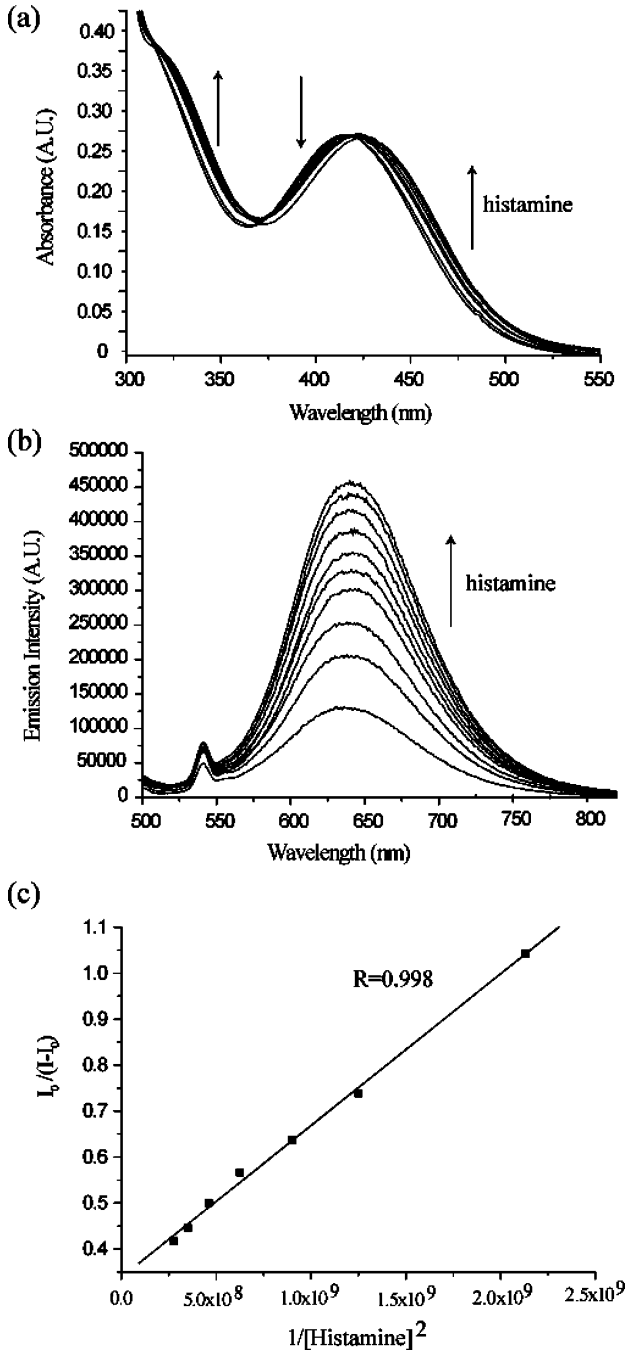

Figure 3. UV−vis spectroscopic and spectrofluorimetric titrations of **Ru_2Eu-1** (3.33×10^{-5} M) with histamine (0 to 6.67×10^{-5} M). All titrations were carried out in EtOH at 298 K with excitation at 466 nm. The slope and *y*-intercept are 3.38×10^{-1} and 3.30×10^{-10} M^2, respectively, of the best fitted $I_0/(I - I_0)$ versus 1/[histamine]^2 plot with log $K = 4.51 \pm 0.03$ at 644 nm.

from 417 to 435 nm (Figure 3a) and the ^{3}MLCT emissions from 644 to 654 nm with a significant enhancement in intensity (Figure 3b). The slope and *y*-intercept were calculated as 3.38×10^{-1} and 3.30×10^{-10} M^2, respectively, by plotting the best fitted $I_0/(I - I_0)$ versus 1/[histamine]^2 graph (Figure 3c). The formation constant (log *K*) of **Ru_2Eu-1** toward putrescine was determined as 4.51 ± 0.03 by fitting the titration curves with the 1:2 Benesi−Hildebrand equation (eq 4). In view of that, each Eu(III) center in **Ru_2Eu-1** was expected to bind two molecules of histamine.

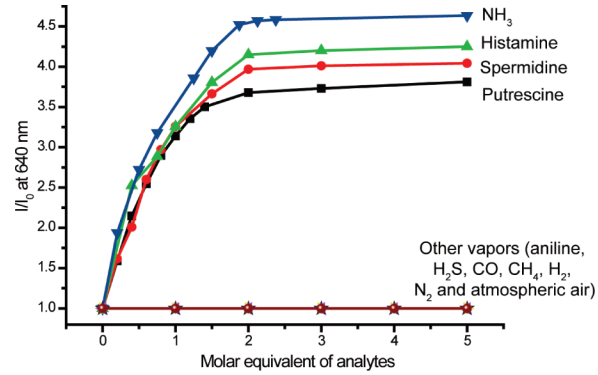

Figure 4. Summary of spectrofluorometric titration (I/I_0 at 640 nm) of **Ru_2Eu-1** (1.0×10^{-4} M) to putrescine, histamine, spermidine, aniline, ammonia, H_2S, CO, CH_4, H_2, N_2, and atmospheric air monitored as a function of the increase in their concentration. All titrations were carried out in ethanol at 298 K.

Table 2. Summaries of the Formation Constants (log *K*) and Detection Limits of Ru_2Eu-1 with Histamine, Putrescine, Spermidine, Aniline, Ammonia, H_2S, CO, CH_4, H_2, N_2, and Atmospheric Air in EtOH at 298 K

	log *K*	detection limit
putrescine[a]	4.86 ± 0.02	27 ppb
spermidine[a]	4.72 ± 0.01	10 ppb
histamine[a]	4.51 ± 0.03	30 ppb
NH_3[a]	4.58 ± 0.03	79 ppb
aniline[a]	1.61 ± 0.08	89 ppm
other common vapors (H_2S, CO, CH_4, H_2, N_2, and atmospheric air)	*b*	*c*

[a] Formation constants (log *K*) of **Ru_2Eu-1** toward various analytes were determined by plotting the best fitted $I_0/(I - I_0)$ vs 1/[analyte]^2 with 1:2 Benesi−Hildebrand equation (eq 4). [b] Formation constants (log *K*) were too small to be detected. [c] Detection limits were unable to calculated.

Figure 4 summarizes the spectrofluorimetric titrations (mole ratio plot) of **Ru_2Eu-1** (1.0×10^{-4} M) with common volatile analytes including biogenic amines (histamine, putrescine, spermidine, and aniline) and other common gases (ammonia, H_2S, CO, CH_4, H_2, N_2, and atmospheric air). Among all the analytes, only those with aliphatic amino functionality (histamine, putrescine, spermidine, and ammonia) are able to induce the spectrofluorometric responses. Aromatic amino functionality and other common moieties are not able to induce any observable spectrofluorometric changes. It is envisioned that **Ru_2Eu-1** can also respond to other aliphatic amino-containing molecules. Spectrofluorimetric titrations (mole ratio plot) of **Ru_2Eu-1** to histamine, putrescine, spermidine, and ammonia reveal that the maximum response occurs at **Ru_2Eu-1**: biogenic amines in a mole ratio of 1:2. Thus, it further confirmed that each Eu(III) center in **Ru_2Eu-1** binds two molecules of the biogenic amines. The sensitivity of **Ru_2Eu-1** for biogenic amine vapors in the luminescent mode of detection (as 3:1 signal: noise ratio) is at the ppb level. In the case of detecting spermidine, the chemodosimeter can reach 10 ppb. Such performance is the highest sensitivity among the other sensing methods for biogenic amine in the literature.[9,10] Table 2 summarizes the log *K* and the detection limit of **Ru_2Eu-1** with histamine, putrescine, spermidine, aniline, ammonia, and other

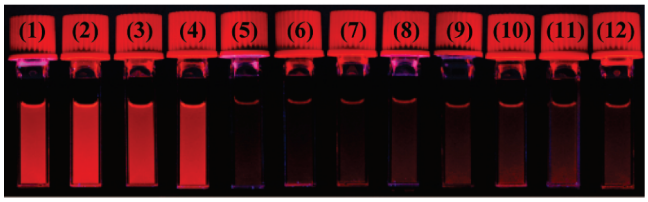

Figure 5. Photographs of the luminometric responses of the **Ru_2Eu-1** (1.0×10^{-4} M) in EtOH at 298 K: (1) **Ru_2Eu-1** + histamine; (2) **Ru_2Eu-1** + putrescine; (3) **Ru_2Eu-1** + spermidine; (4) **Ru_2Eu-1** + NH_3; (5) **Ru_2Eu-1** only; (6) **Ru_2Eu-1** + aniline; (7−12) **Ru_2Eu-1** + H_2S, CO, N_2, CH_4, H_2, and air, respectively. Excitation λ_{ex} = 365 nm.

common vapors (H_2S, CO, CH_4, H_2, N_2, and atmospheric air) in EtOH at 298 K.

Biogenic amines are famous for their distinct and disguising odor. Rapid detecting of biogenic amines in their vapor form and reporting the signal in a naked-eyed manner is particularly important for the seafood industry. Naked-eyed luminometric responses of **Ru_2Eu-1** toward various amine vapors and gaseous analytes were demonstrated and monitored by purging their gaseous vapors under 1 atm. A 3 mL sample of each vapor of histamine, aniline, putrescine, spermidine, gaseous NH_3, H_2S, CO, CH_4, H_2, N_2, and atmospheric air were purged into the headspace of the ethanolic solutions of **Ru_2Eu-1** (2.0×10^{-4} M) at 298 K. The purging volume was for all of these analytes. Figure 5 shows the photographs of the naked-eyed luminometric responses of the **Ru_2Eu-1** toward different vapors and gaseous amines.

Specificity of Ru_2Eu-1 toward Histamine, Putrescine, Spermidine, and Gaseous NH_3. The close resemblance of the UV−vis and luminescent responses of the "**Ru_2Eu-1**−biogenic amine" mixtures to those of $K_2[Ru(^tBubpy)(CN)_4]$ suggest that the cyanide bridges between Ru(II) and Eu(III) of the trinuclear complex are cleaved after the binding of the biogenic amine vapors to the Eu(III) centers. The subsequent observation of $\{K[Ru(^tBubpy)(CN)_4]\}^-$ (m/z 513 $[M + K]^-$) and $[Eu(histamine)_2(H_2O)_2(OH)_2]^+$ (m/z 445) in the electrospray ionization mass spectrometry (ESI-MS) of **Ru_2Eu-1**−biogenic amine mixtures further confirmed the suggestion. The substrate selectivity of the binding-induced dissociation is most probably attributable to the preferential coordination of amino functionalities to Eu(III). Figure 6 shows the proposed recognition and signaling mechanism of **Ru_2Eu-1** toward specific biogenic amine vapors.

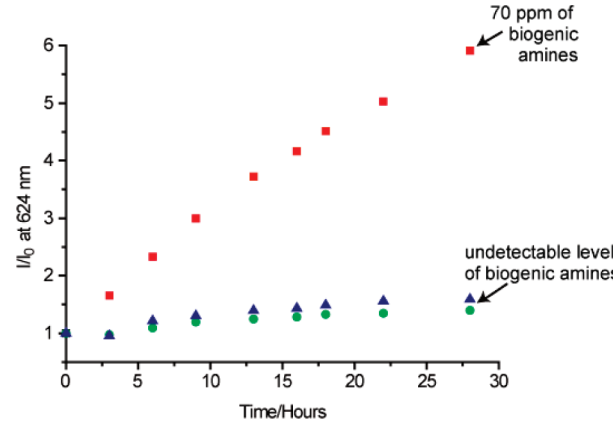

Figure 7. Summary of spectrofluorometric titration (I/I_0 at 624 nm) of **Ru_2Eu-1** (3.33×10^{-5} M) to 20.0 g of homogenized Atlantic mackerel (*Scomber scombrus*) fish samples at conditions of (■) storing at room temperature, (●) storing at 0 °C, and (▲) storing with 60 g of preservative monitored as a function of time. All titrations were carried out in ethanol at 298 K. The total concentrations of biogenic amines (putrescine, cadaverine, histamine, and spermidine) were determined by GC/MS analyses.[27]

Detection of Gaseous Biogenic Amines in Fish Sample by Ru_2Eu-1. For final verification of the chemodosimetric idea, **Ru_2Eu-1** was used to examine the freshness of fish sample, Atlantic mackerel (*Scomber scombrus*). A 20.0 g sample of fresh Atlantic mackerel loin was homogenized and kept and sealed in a 50 mL glass container. According to the storing time, 3 mL of gaseous vapor from the headspace of the fish filling container was taken and injected into the ethanolic solution of **Ru_2Eu-1**. Luminescent responses (I/I_0) of **Ru_2Eu-1** were recorded as a function of time with respect to three different storing conditions, i.e., room temperature, frozen temperature (0 °C), and room temperature with 60 g of preservatives ($NaNO_2$). Figure 7 summarizes the spectrofluorimetric titrations of **Ru_2Eu-1** (3.33×10^{-5} M) with the vapor of the headspace in those three storage conditions. Among all the conditions, only the fish sample stored at room temperature showed an enhancement of spectrofluorimetric response as an increase of storage time. However, the fish samples stored at frozen conditions and with preservative are not able to induce any observable spectrofluorimetric changes upon an increase of the storage time. The results were understandable because when fish are exposed to elevated temperatures for an extended period of time, spoilage bacteria can grow and produce an

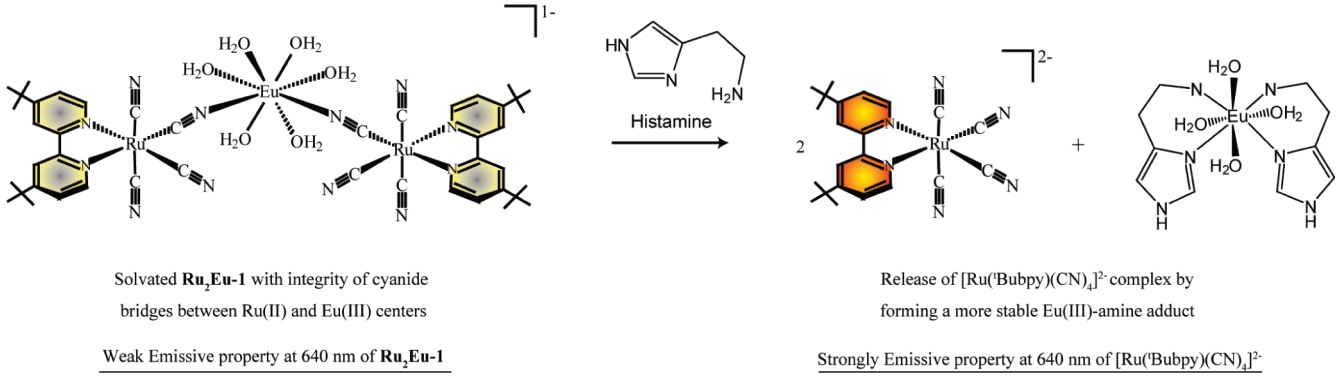

Figure 6. Proposed molecular recognition and luminescence signaling mechanism.

enzyme that can change amino acids into biogenic amines.e-h Lowering the temperature or adding preservative as quickly as possible will prevent these bacteria from growing and producing those biogenic amines. The most prevalent biogenic amines found in Atlantic mackerel are histamine, putrescine, spermidine, and cadaverine. Gas chromatography mass spectrometry (GC/MS) was used as a reference to determine the concentration of biogenic amines in the homogenized fish samples. GC/MS analyses[27] (SI Figure 7) showed that the fish sample contained putrescine, cadaverine, histamine, and spermidine, with retention times 10.8, 11.4, 11.8, and 15.5 min, respectively, after 30 h of storage at room temperature. The concentration of these four biogenic amines was calculated as 70 ppm. It is worth noting that 50 ppm of histamine was classified as the borderline of the freshness of fish.[28] Furthermore, GC/MS analyses showed that there were no biogenic amines in the fish samples either in storage at frozen temperature or in storage with 60 g of preservative.

CONCLUSION

A new heterobimetallic Ru(II)−Ln(III) donor−acceptor complex **Ru_2Eu-1** has been synthesized and characterized. Its photophysical and crystallographic data were reported. **Ru_2Eu-1** was found to be the first colorimetric and luminescent chemodosimeter selective for biogenic amine vapors with detection limit down to 10 ppb. The sensitivity of the described chemodosimetric assay seemed to be a more convenient and easier method than the traditional analytical analysis as well as the typical mammalian sense of smell. This chemodosimetric detection is able to detect these scombrotoxin original biogenic amines. The heterobimetallic chemodosimetric compound approach, where one metal center which acts as a functional-specific binding site is bridged to another metal center responsible for signal transduction, seems to be a versatile way of designing new chemodosimeters and chemosensors.

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ACKNOWLEDGMENT

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SUPPORTING INFORMATION AVAILABLE

Crystallographic data of **Ru_2Eu-1**. Mole ratio plot, ESI-MS UV−vis spectroscopic and spectrofluorometric titrations, and GC/MS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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