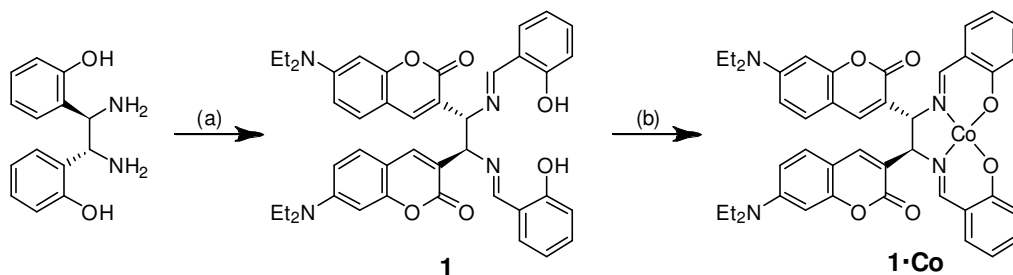


## Supporting Information

### Fluorescence Turn-On Sensor for Cyanide Based on a Cobalt(II)-Coumarinylsalen Complex

Jae Han Lee, A Reum Jeong, Ik-Soo Shin, Hae-Jo Kim and Jong-In Hong



**Scheme 1:** (a) 2 equiv coumarine aldehyde, methanol, (b) Co(OAc)<sub>2</sub>, TEA, dichloromethane/methanol

#### 1. Synthesis of **1-Co**

##### Synthesis of **1**

To a solution of 7-diethylamino-coumarin-3-carboxaldehyde (490 mg, 2.00 mmol) in 2.0 mL of dichloromethane was added a yellow slurry solution of 2,2'-dihydroxyphenylenediamine (244 mg, 1.00 mmol) in 3.0 mL of methanol. Resulting clear solution was further stirred overnight at rt to afford yellow precipitates. The precipitates were filtered and washed with 1.0 mL of methanol and dried to afford the desired rearranged diimine as a yellow solid in 85 % yield.

400 MHz <sup>1</sup>H NMR in DMSO-d<sub>6</sub>: δ (ppm, 2.50) 13.20 (br, 2H of RAHB OH); 8.55 (s, 2H of imine H), 7.79 (s, 2H of coumarin H), 7.37 (m, 4H of Ar H); 7.26 (td, <sup>3</sup>J = 8.4 Hz, <sup>4</sup>J = 1.6 Hz, 2H of Ar H); 6.80 (m, 4H of Ar H); 6.60 (dd, <sup>3</sup>J = 8.8 Hz, <sup>4</sup>J = 2.4 Hz, 2H of Ar H); 6.40 (d, <sup>4</sup>J = 2.4 Hz, 2H of Ar H); 5.21 (s, 2H of C\*H); 3.34 (q, <sup>3</sup>J = 7.2 Hz, 4H of NCH<sub>2</sub>CH<sub>3</sub>); 1.04 (q, <sup>3</sup>J = 7.2 Hz, 6H of NCH<sub>2</sub>CH<sub>3</sub>). 400 MHz <sup>1</sup>H NMR in CD<sub>2</sub>Cl<sub>2</sub>: δ (ppm, 5.30) 13.24 (br, 2H of RAHB OH); 8.44 (s, 2H of imine H), 7.67 (s, 2H of coumarin H), 7.24 (m, 6H of Ar H); 6.91 (d, <sup>3</sup>J = 8.0 Hz, 2H of Ar H); 6.81 (t, <sup>3</sup>J = 8.0 Hz, 2H of Ar H); 6.53 (dd, <sup>3</sup>J = 8.8 Hz, <sup>4</sup>J = 2.4 Hz, 2H of Ar H); 6.41 (d, <sup>4</sup>J = 2.4 Hz, 2H of Ar H); 5.28 (s, 2H of C\*H); 3.36 (q, <sup>3</sup>J = 6.8 Hz, 4H of NCH<sub>2</sub>CH<sub>3</sub>); 1.15 (q, <sup>3</sup>J = 6.8 Hz, 6H of NCH<sub>2</sub>CH<sub>3</sub>). 100 MHz <sup>13</sup>C NMR in CD<sub>2</sub>Cl<sub>2</sub>: δ (ppm, 53.6) 167.3, 161.5, 161.29, 156.2, 150.9, 142.1, 132.7, 132.1, 129.3, 118.86, 118.81, 118.79, 116.93, 109.1, 108.3, 96.9; 70.6, 44.9, 12.36

HRMS (ESI<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>) *m/z* cal'd for C<sub>42</sub>H<sub>43</sub>N<sub>4</sub>O<sub>6</sub> 699.3177, obs'd 699.3193 [M+H]<sup>+</sup>  
[α]<sub>D</sub><sup>25</sup> +39.5 (c 0.01) for (S,S)-1

##### Synthesis of **1-Co**

To a solution of **1** (69.8 mg, 0.100 mmol) in 1.0 mL of dichloromethane was added a slurry solution of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (21.9 mg, 0.100 mmol) in 0.5 mL of methanol and triethylamine (0.2 mL). Resulting clear solution was further stirred for 1 hr at rt. All the volatiles are removed under reduced pressure and resulting solid was recrystallized in MeOH/CH<sub>2</sub>Cl<sub>2</sub> to afford the desired metal complex as a brown solid in 90 % yield.

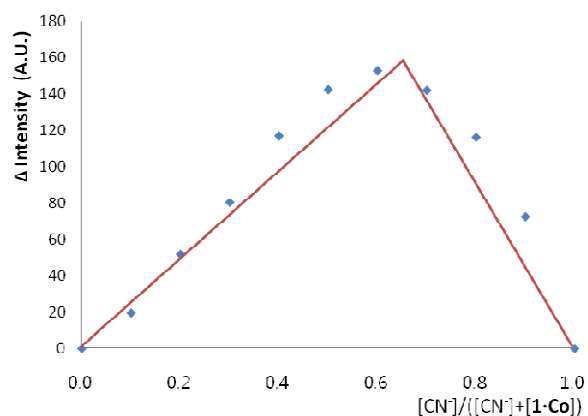
HRMS (ESI<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>) *m/z* cal'd for C<sub>42</sub>H<sub>40</sub>N<sub>4</sub>O<sub>6</sub>Co 755.2274, obs'd 755.2311 [M]<sup>+</sup>

##### Confirmation of **1-Co**·2CN<sup>-</sup>

To a solution of **1-Co** (1.0 mg, 1.32 mmol) in 1.0 mL of acetonitrile was added 10 equivalent tetrabutylammonium cyanide (3.5 mg, 13.2 mmol) in 1.0 mL of acetonitrile. Resulting clear solution was stirred for a while and analyzed by mass spectroscopy.

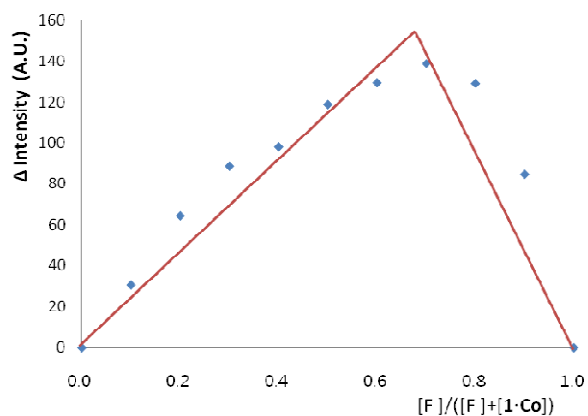
HRMS (FAB<sup>-</sup>, m-NBA) *m/z* cal'd for C<sub>44</sub>H<sub>40</sub>CoN<sub>6</sub>O<sub>6</sub> 807.2341, obs'd 803.2341 [M]<sup>-</sup>

## 2. Job's Plot between 1·Co and Cyanide



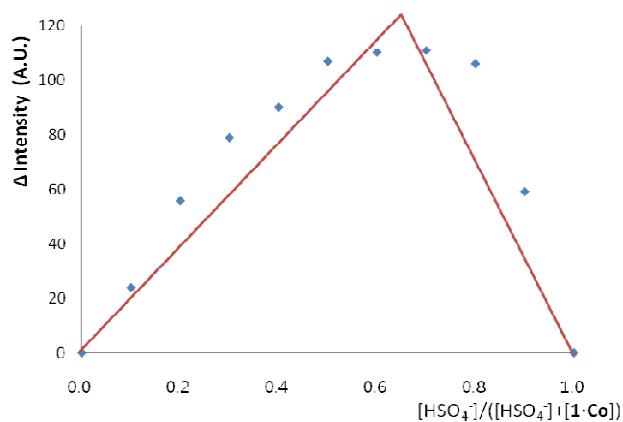
**Figure S1.** Job's plot between cobalt(II)-salen and cyanide,  $[1 \cdot Co] + [CN^-] = 20 \mu M$ . It confirms 1:2 binding mode.

## 3. Job's Plot between 1·Co and Fluoride



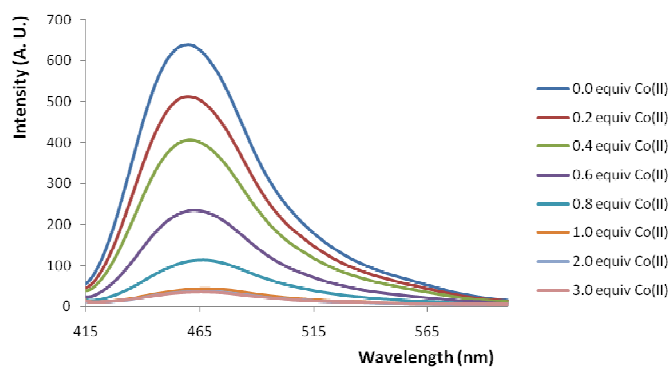
**Figure S2.** Job's plot between cobalt(II)-salen and fluoride,  $[1 \cdot Co] + [F^-] = 20 \mu M$ . It confirms 1:2 binding mode.

## 4. Job's Plot between 1·Co and Hydrogen Sulfate



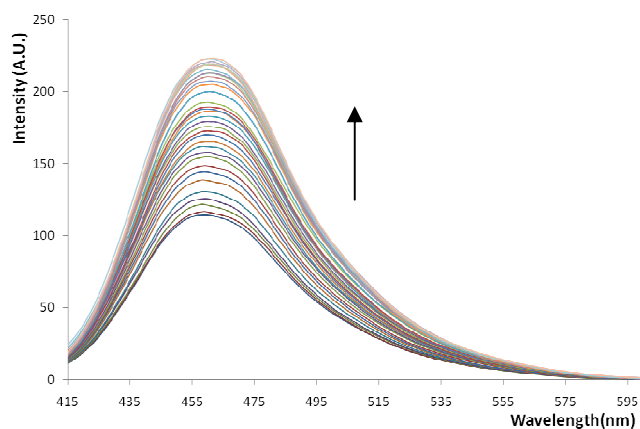
**Figure S3.** Job's plot between cobalt(II)-salen and hydrogen sulfate,  $[1 \cdot Co] + [HSO_4^-] = 20 \mu M$ . It confirms 1:2 binding mode.

## 5. Fluorescence Change of **1** upon the addition of Co(II)



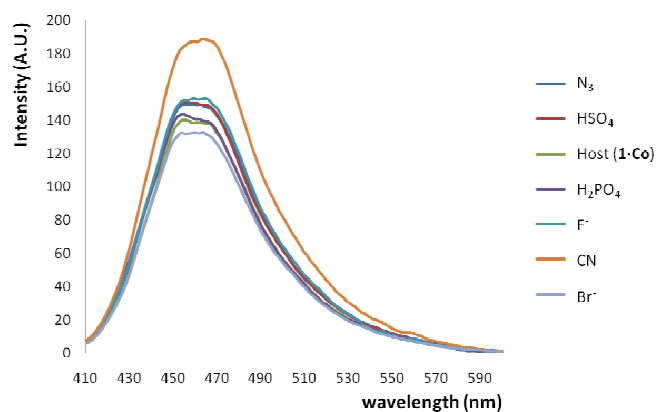
**Figure S4.** Fluorescence emission of **1** (5  $\mu$ M, MeCN) in the presence of various concentration of Co(II) (0~15  $\mu$ M).

## 6. Fluorescent binding assay of **1**•Co with cyanide in acetonitrile at 25 °C



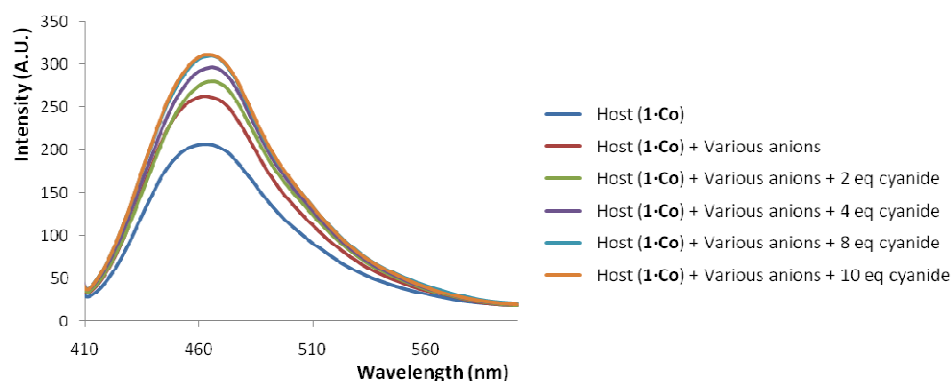
**Figure S5.** Fluorescence spectra obtained by the addition of cyanide (0 ~ 21.9  $\mu$ M) to **1**•Co (5  $\mu$ M) in acetonitrile.

## 7. Fluorescence change of **1**•Co upon the addition of various anions



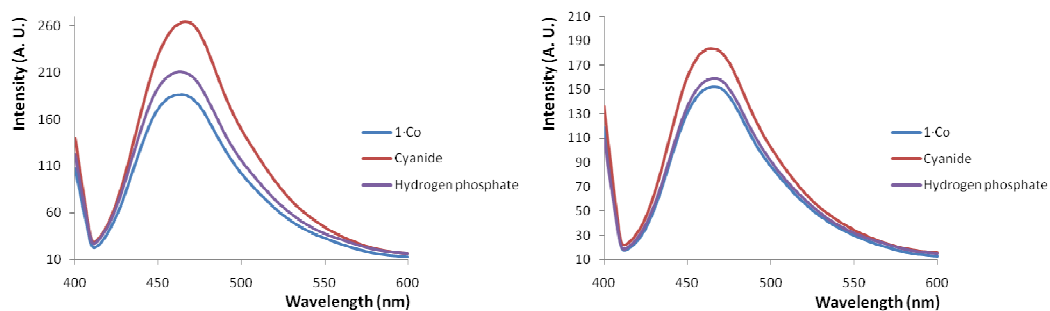
**Figure S6.** Fluorescence emission of **1**•Co (5  $\mu$ M, MeCN) in the presence of various anions (each 10  $\mu$ M).

## 8. Fluorescence change upon the addition of cyanide anion in the presence of various anions



**Figure S7.** Fluorescence change of **1-Co** (5  $\mu$ M, MeCN) upon the addition of cyanide anion in the presence of various anions ( $\text{HSO}_4^-$ ,  $\text{N}_3^-$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{H}_2\text{PO}_4^-$ , 5  $\mu$ M each).

## 9. Effect of water content on sensing cyanide using **1-Co**

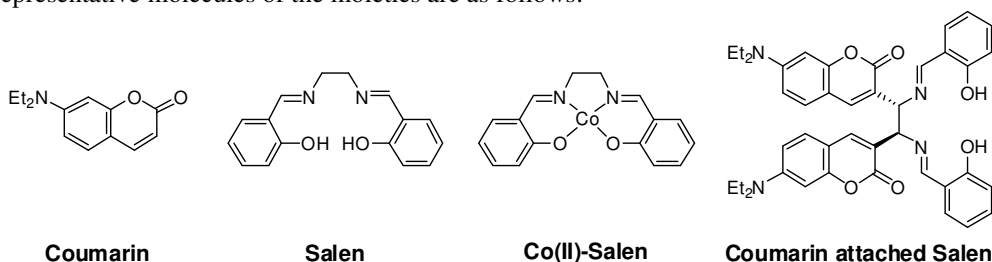


**Figure S8.** Fluorescence changes of **1-Co** (left: 5  $\mu$ M, MeCN, right: 5% water in  $\text{CH}_3\text{CN}$ ) upon the addition of  $\text{HSO}_4^-$  and  $\text{CN}^-$  (20  $\mu$ M each).

## 10. Electrochemistry

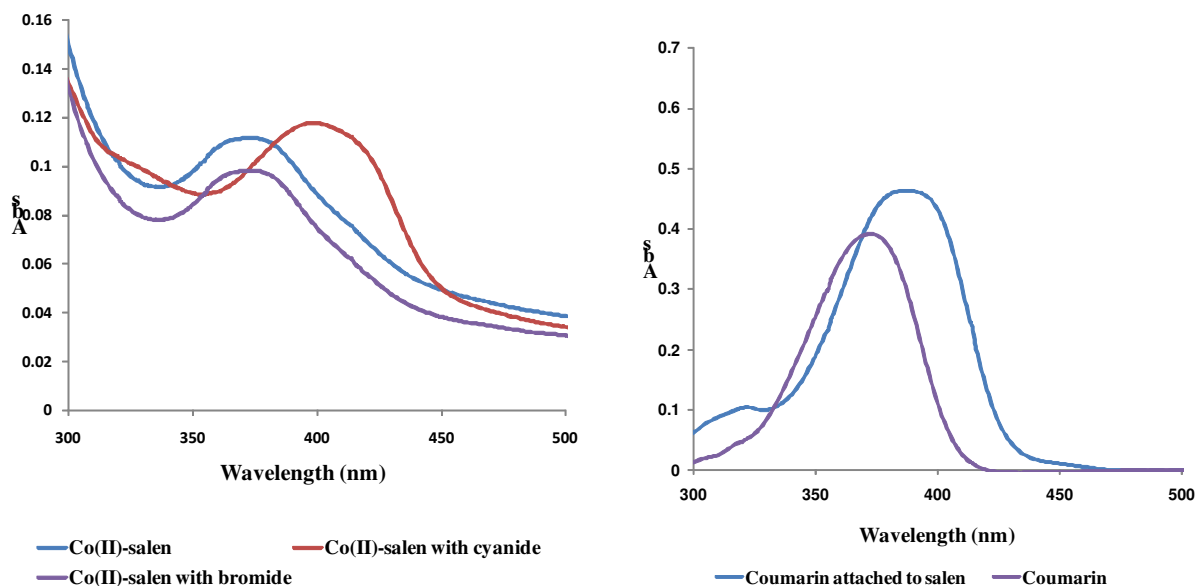
Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed using a CH Instruments 650B Electrochemical Analyzer (CH Instruments, Inc., Texas, USA). All electrochemical studies were referenced with respect to an Ag/Ag<sup>+</sup> reference electrode. All potential values were calibrated against the saturated calomel electrode (SCE) by measuring the oxidation of ferrocene as an internal reference ( $E^{\circ}(\text{Fc}^+/\text{Fc}) = 0.424 \text{ V vs SCE}$ )<sup>1</sup>. A platinum (Pt) disk (diameter: 2 mm) working electrode was used for electrochemical studies. It was polished with 0.05  $\mu\text{M}$  alumina (Buehler, Illinois, USA) on a felt pad and sonicated in absolute ethanol and deionized water mixed solution (1:1 v/v) for 5 min. Then it was rinsed with ethanol and deionized water subsequently. Then the electrode was blew with N<sub>2</sub> gas for 2 min. Solutions were prepared with adding All the electrochemical samples were purged with Ar gas for 15 min and were measured under Ar atmosphere. Basically, CV was performed on DMF solution samples with 0.1 M tetramethylammonium hexafluorohpsphate (TMAPF<sub>6</sub>) as a supporting electrolyte, but DPV was also applied to the samples which didn't show quasi-reversible redox behaviors.

As determined by Nagano and co-workers, the experiments were performed using the moieties that consist of **1·Co**. The representative molecules of the moieties are as follows:



(1). Masui, M.; Sayo, H.; Tsuda, Y., J. Chem. Soc. B 1968, 973.

### □ UV-Vis spectra

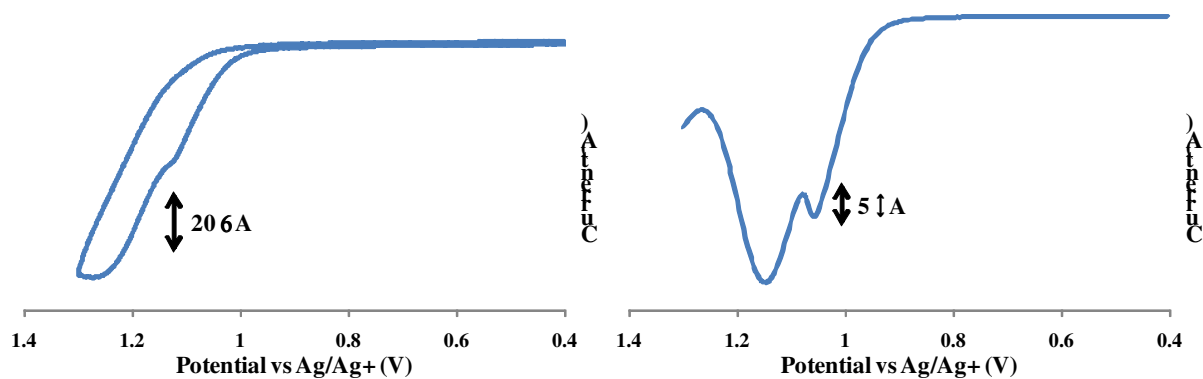


**Figure S9.** left : UV-Vis absorption of Co(II)-Salen(25  $\mu\text{M}$ , MeCN) in the presence of various anions(125  $\mu\text{M}$ ). right : UV-Vis absorption of coumarin attached to salen(8  $\mu\text{M}$ ) and coumarin(16  $\mu\text{M}$ )

### □ Cyclic Voltammogram and differential pulse voltammogram of coumarin attached to salen (1 mM)

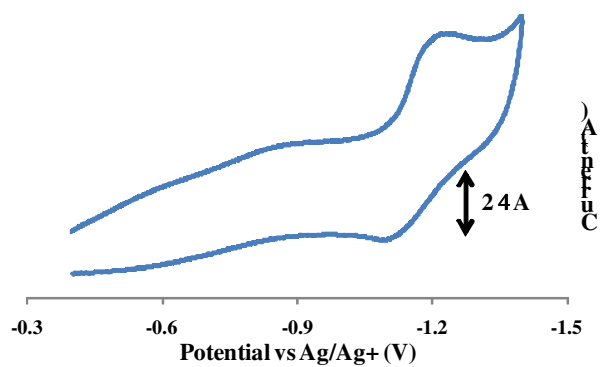
HOMO :  $-5.66 \text{ eV}$  / LUMO :  $-2.46 \text{ eV}$

It is representative of the coumarin moiety in **1·Co** rather than coumarin shown in ⑥ because the coumarin shown in □ is not affected by intramolecular dipole-dipole interaction between coumarins in **1·Co**. Additionally, It is confirmed that salen has no potential in the experimented region from the spectrum shown in ⑦.



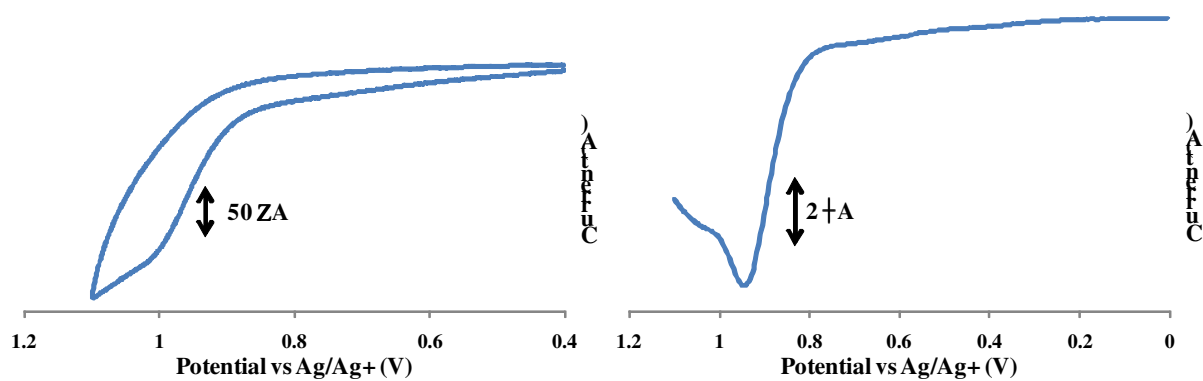
□ Cyclic voltammogram of Co(II)-salen (1 mM) without anions

HOMO : -6.74 eV / LUMO : -3.36 eV



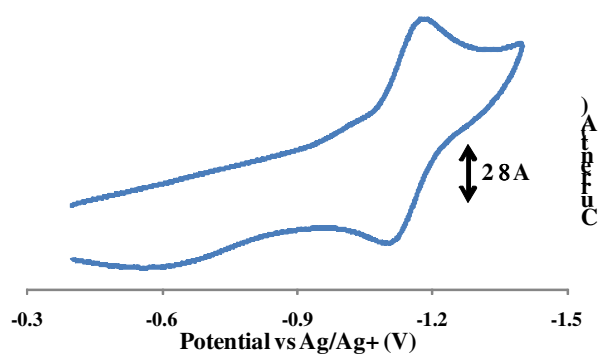
□ Cyclic voltammogram and differential pulse voltammogram of Co(II)-salen (1 mM) with  $\text{CN}^-$  (20 mM)

HOMO : -5.46 eV / LUMO : -2.35 eV



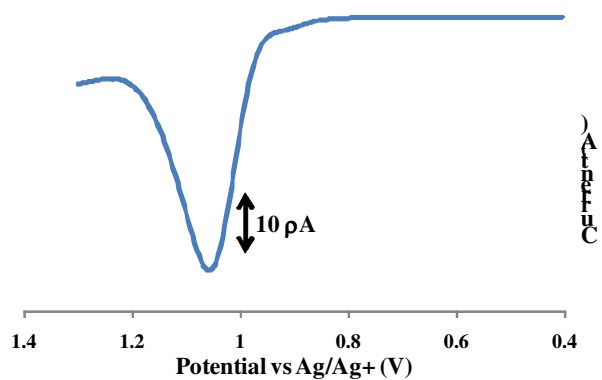
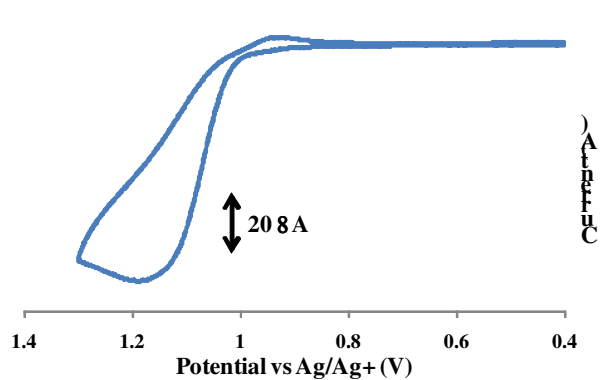
□ Cyclic Voltammogram of Co(II)-salen (1 mM) with  $\text{Br}^-$  (20 mM)

HOMO : -6.71 eV / LUMO : -3.37 eV

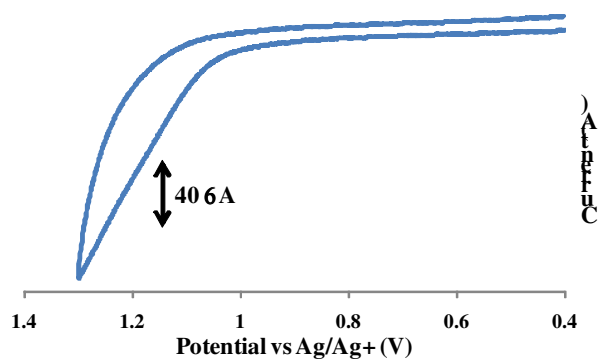


□ Cyclic voltammogram and differential pulse voltammogram of coumarin (2 mM)

HOMO :  $-5.57$  eV / LUMO :  $-2.24$  eV



□ Cyclic Voltammogram of salen



## 11. Mathematical bases for programming

A model reaction between a recognition moiety (H) and an analyte (G), in a 1:2 stoichiometry, is assumed to be in equilibrium as follows;



The equilibrium constants for the processes are expressed as the ratio of product over reactants.

$$K_1=[HG]/[H][G] \quad (3)$$

$$K_2=[HG_2]/[HG][G] \quad (4)$$

The fluorescence intensity in this process can be defined as eq 5. F and  $\alpha$  correspond to the fluorescence intensities and mole fractions of subscript species, respectively.

$$F_{cal}=F_H \alpha_H + F_{HG} \alpha_{HG} + F_{HG_2} \alpha_{HG_2} \quad (5)$$

If one solves for [G] from eq 3 and eq 4 as a function of total host [H]<sub>T</sub> and total guest [G]<sub>T</sub> concentrations, eq 6 is obtained.

$$K_1K_2[G]^3 + (2K_1K_2[H]_T - K_1K_2[G]_T + K_1)[G]^2 + (K_1[H]_T - K_1[G]_T + 1)[G] - [G]_T = 0 \quad (6)$$

Equations 7, 8 and 9 give [H], [HG] and [HG<sub>2</sub>], respectively, as a function of [G]

$$[H] = [H]_T / (1 + K_1[G] + K_1K_2[G]^2) \quad (7)$$

$$[HG] = K_1[G][H]_T / (1 + K_1[G] + K_1K_2[G]^2) \quad (8)$$

$$[HG_2] = K_1K_2[G]^2 [H]_T / (1 + K_1[G] + K_1K_2[G]^2) \quad (9)$$

1> Equation 9

From Equation (3) and (4);  $[HG]/[H]=K_1[G]$ ,  $[HG_2]/[H] = K_1K_2[G]^2$

Mole fraction of HG and HG<sub>2</sub> is followings;

$$\alpha_{HG} = \frac{[HG]}{[H] + [HG] + [HG_2]} = \frac{([HG]/[H])}{1 + ([HG]/[H]) + ([HG_2]/[H])} = \frac{K_1[G]}{1 + K_1[G] + K_1K_2[G]^2}$$

$$\alpha_{HG_2} = \frac{[HG_2]}{[H] + [HG] + [HG_2]} = \frac{([HG_2]/[H])}{1 + ([HG]/[H]) + ([HG_2]/[H])} = \frac{K_1K_2[G]^2}{1 + K_1[G] + K_1K_2[G]^2}$$

In a 1:2 stoichiometry, the mass balance is ;

$$[G] = [G_T] - [HG] - 2[HG_2] = [G_T] - \frac{K_1[G][H]_T}{1 + K_1[G] + K_1K_2[G]^2} - \frac{2K_1K_2[G]^2[H]_T}{1 + K_1[G] + K_1K_2[G]^2}$$

Setting the equation equal to zero and combining the linear terms now provide the cubic function below :

$$K_1K_2[G]^3 + (2K_1K_2[H]_T - K_1K_2[G]_T + K_1)[G]^2 + (K_1[H]_T - K_1[G]_T + 1)[G] - [G]_T = 0$$

2> Finding real root (Newton-Raphson Method)

$$F(G) = K_1K_2[G]^3 + (2K_1K_2[H]_T - K_1K_2[G]_T + K_1)[G]^2 + (K_1[H]_T - K_1[G]_T + 1)[G] - [G]_T$$

In upper functions;

$$F(0) = -[G]_T \leq 0$$

$$F(G_T) = 2K_1K_2[G_T]^2[H]_T + K_1[G_T][H]_T \geq 0$$

It is necessary that only one root exists between 0 and G<sub>T</sub>. From above two inequalities, there is one root among three roots of equation 9 at least between 0 and G<sub>T</sub>. Other two roots have same sign because multiplication between



three roots are positive value; one has negative value and other also has negative values. Where other two roots have negative sign, it is clear that only one root exist between 0 and  $G_T$ . Where other two roots have positive sign, it is unclear that only one root exists between 0 and  $G_T$ . However, it can be elucidated by simple mathematical proof. Therefore, the Newton-Raphson method is used for finding real root of equation 9 because it is fast and effective in this case.

### 3> Finding Fluorescent Constant for HG and $HG_2$ (Gauss Elimination Method)

The fluorescence intensity is defined as following :

$$F_{cal} = F_0\alpha_H + F_{HG}\alpha_{HG} + F_{HG_2}\alpha_{HG_2}$$

Optimal fluorescent constants for HG and  $HG_2$  are needed and found. The standard of optimal fluorescent constants is amount that is summed every square of difference between observed and calculated fluorescence intensity.

$$S_r = \sum (F_{obs} - F_{cal})^2 = \sum (F_{obs} - F_0\alpha_H + F_{HG}\alpha_{HG} + F_{HG_2}\alpha_{HG_2})^2$$

To be the minimum  $S_r$  value, the partial differential with respect to  $F_{HG}$  and  $F_{HG_2}$  are zero.

$$\frac{\partial S_r}{\partial F_{HG}} = 2 \sum (F_{obs} - F_0\alpha_H - F_{HG}\alpha_{HG} - F_{HG_2}\alpha_{HG_2})\alpha_{HG} = 0$$

$$\frac{\partial S_r}{\partial F_{HG_2}} = 2 \sum (F_{obs} - F_0\alpha_H - F_{HG}\alpha_{HG} - F_{HG_2}\alpha_{HG_2})\alpha_{HG_2} = 0$$

These equations are converted as following:

$$\sum (F_{obs} \alpha_{HG}) - \sum (F_0 \alpha_H \alpha_{HG}) = \sum (F_{HG} \alpha_{HG}^2) + \sum (F_{HG_2} \alpha_{HG} \alpha_{HG_2})$$

$$\sum (F_{obs} \alpha_{HG_2}) - \sum (F_0 \alpha_H \alpha_{HG_2}) = \sum (F_{HG} \alpha_{HG} \alpha_{HG_2}) + \sum (F_{HG_2} \alpha_{HG_2}^2)$$

These equations are converted as following matrix:

$$\begin{pmatrix} \sum (F_{obs} \alpha_{HG}) - \sum (F_0 \alpha_H \alpha_{HG}) \\ \sum (F_{obs} \alpha_{HG_2}) - \sum (F_0 \alpha_H \alpha_{HG_2}) \end{pmatrix} = \begin{pmatrix} F_{HG} \\ F_{HG_2} \end{pmatrix} \begin{pmatrix} \sum (\alpha_{HG}^2) + \sum (\alpha_{HG} \alpha_{HG_2}) \\ \sum (\alpha_{HG} \alpha_{HG_2}) + \sum (\alpha_{HG_2}^2) \end{pmatrix}$$

The matrix can be solved by Gauss elimination method.

## 12. Programming by C Language

This program contains four sections. Section one reads the input data. This consists of: (a) the concentrations of the guests; (b) the expected ranges of  $K_1$  and  $K_2$  values; (c) the measured fluorescent intensities according to the guest concentrations.

Section two of the program consists of subroutine which utilizes the input data from section one to perform three tasks. First, it calculates the concentration of all species present in solution using the stability constants from section one. The equations 6-9 is used to calculate the concentration of all free and complexed species and the equation 6 is solved by Newton-Raphson method.<sup>1</sup> The program then calculates the optimal fluorescent constants for complexed species using Gaussian elimination method<sup>2</sup>. And the expected fluorescent intensities is calculated using equation 5 to account for the presented data from prior procedure. Finally, the program finds out and prints best-fit association constant values as well as other parameters showing a minimum deviation from the observed fluorescence intensity.

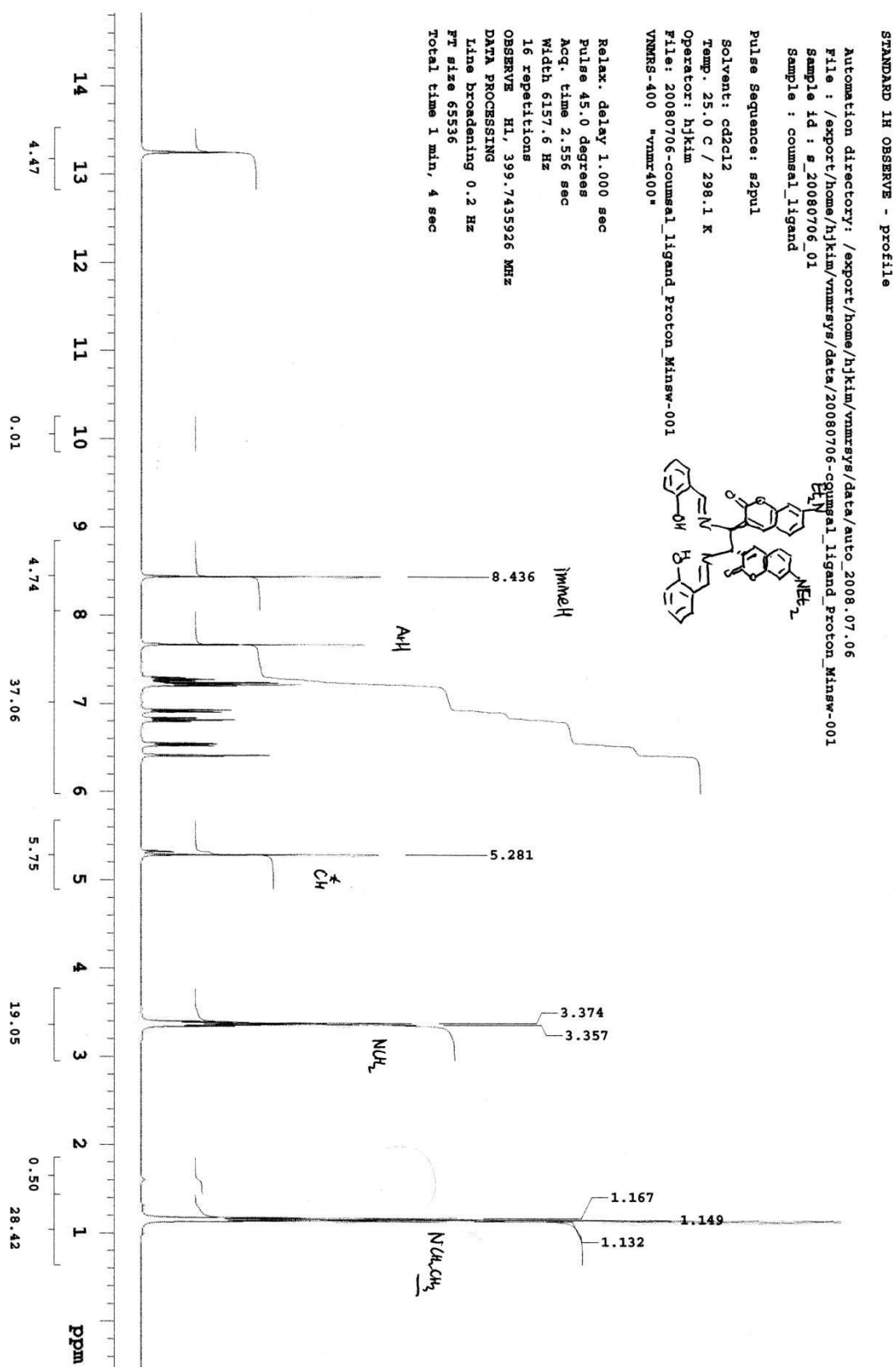
Section three of the program includes the input data from section two to produce a plot of calculated data. This consists of: (a) the concentrations of the various guests; (b) the best-fit association constants; (c) the best-fit fluorescence constants of free and complexed species; (d) the concentration ranges of the guest together with data pitch.

Section four of the program contains the output routines. Using the input data from section three, this section produce a lot of data points enough to plot a continuous graph of calculated data.

(1) Ypma, T. J. *SIAM Rev.* **1995**, 37, 531.

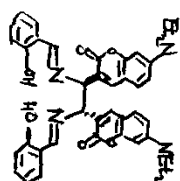
(2) Atkinson, K. A. *An Introduction to Numerical Analysis*, 2nd ed.; John Wiley & Sons: New York, 1989;pp.

### 13. NMR Spectrum



STANDARD 1H OBSERVE - profile

Automation directory: /export/home/hjkim/vnmrsys/data/autc\_2008.07.06  
file: /export/home/hjkim/vnmrsys/data/20080706-coumsal\_ligand\_Dept-001  
sample id: s\_20080706\_01  
sample: coumsal\_ligand



Pulse Sequence: DEPT

CH3 carbons

CH2 carbons

CH carbons

all protonated carbons

