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SUPPORTING INFORMATION

Title: A Diiminoplatinum(ii) Complex of 4-Ethynylbenzo-15-crown-5 as a Luminescent Sensor for Divalent Metal Ions
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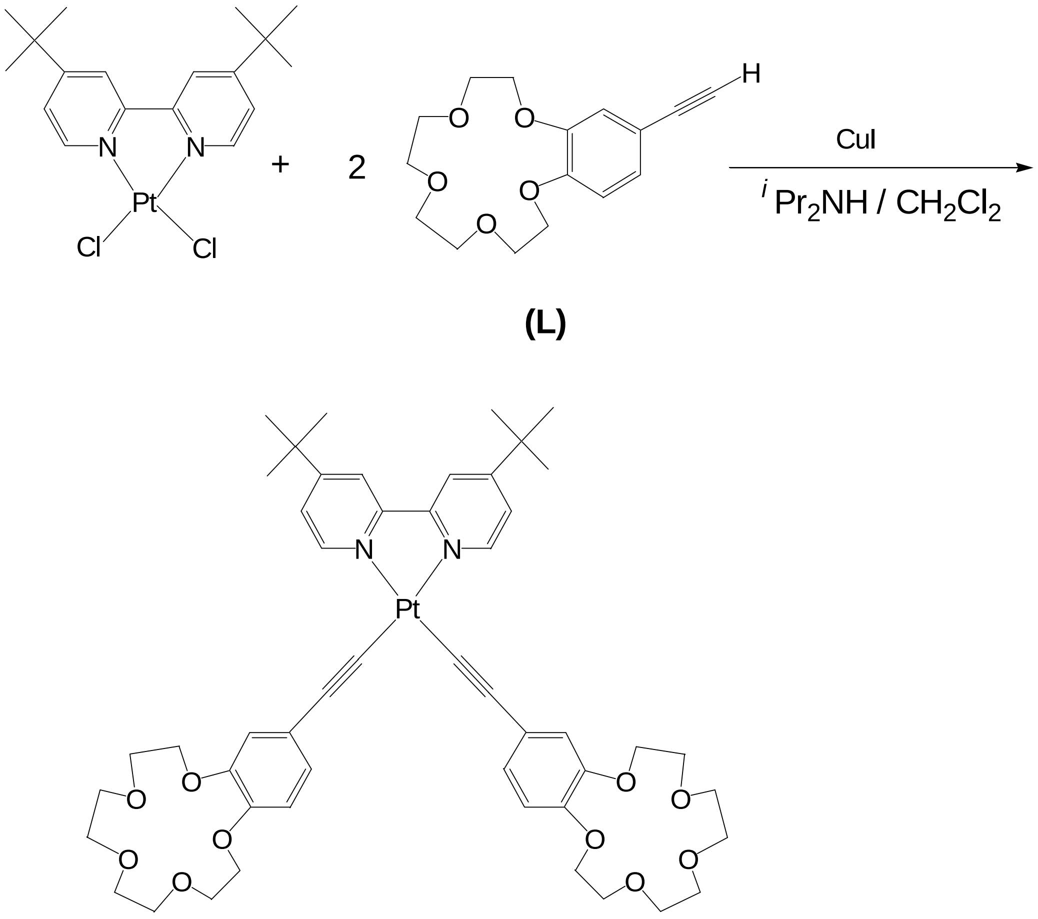
Ref. No.: I03214

Scheme for synthesis of **1**; emission spectral traces of **1** at increasing equivalents of Zn^{2+}, Ca^{2+}, Na^{+} and K^{+} ions; table for fluid-state emissions of **1**–**3** in acetonitrile with 100 equivalents of $M(ClO_4)_x$; analysis of the complexation of ions using nonlinear least-squares fits and Hill plots.

Scheme S1



(L)

(1)

Table S1 Fluid emission data of **1–3** in acetonitrile (complex concentration = 3.2×10^{-5} mol dm^{-3}; λ_{ex} 405 nm) with 100 equivalents of $M(ClO_4)_x$.

Complex	λ_{max} / nm; ϕ	I / I (monitored at λ_{max})
1	635; 1.14×10^{-4}	1
1 + $Mg(ClO_4)_2$	553; 0.075	1035
1 + $Zn(ClO_4)_2$	560; 0.052	870
1 + $Zn(NO_3)_2$	560; 0.021	250
1 + $ZnCl_2$	565; 5.96×10^{-3}	105
1 + $NaClO_4$	600; 1.59×10^{-3}	11
1 + $KClO_4$	610; 4.60×10^{-4}	4
1 + $Cd(ClO_4)_2$	613; 4.06×10^{-4}	3
1 + $Ca(ClO_4)_2$	563; 0.022	300
2	560; 7.87×10^{-4}	1
2 + $Zn(ClO_4)_2$	581; 6.39×10^{-3}	10
3	610; 1.58×10^{-3}	1
3 + $Zn(ClO_4)_2$	610; 1.53×10^{-3}	1

Figure S1. Emission spectral traces and (inset) luminescence enhancement factor (≡ I/I_o; monitored at 560 nm) of **1** at increasing equivalents of $Zn(ClO_4)_2$ in 0.1 M *n*Bu_4NPF_6 acetonitrile solution at 298 K (λ_{ex} = 405 nm, [**1**] = 3.2×10^{-5} mol dm^{-3}).

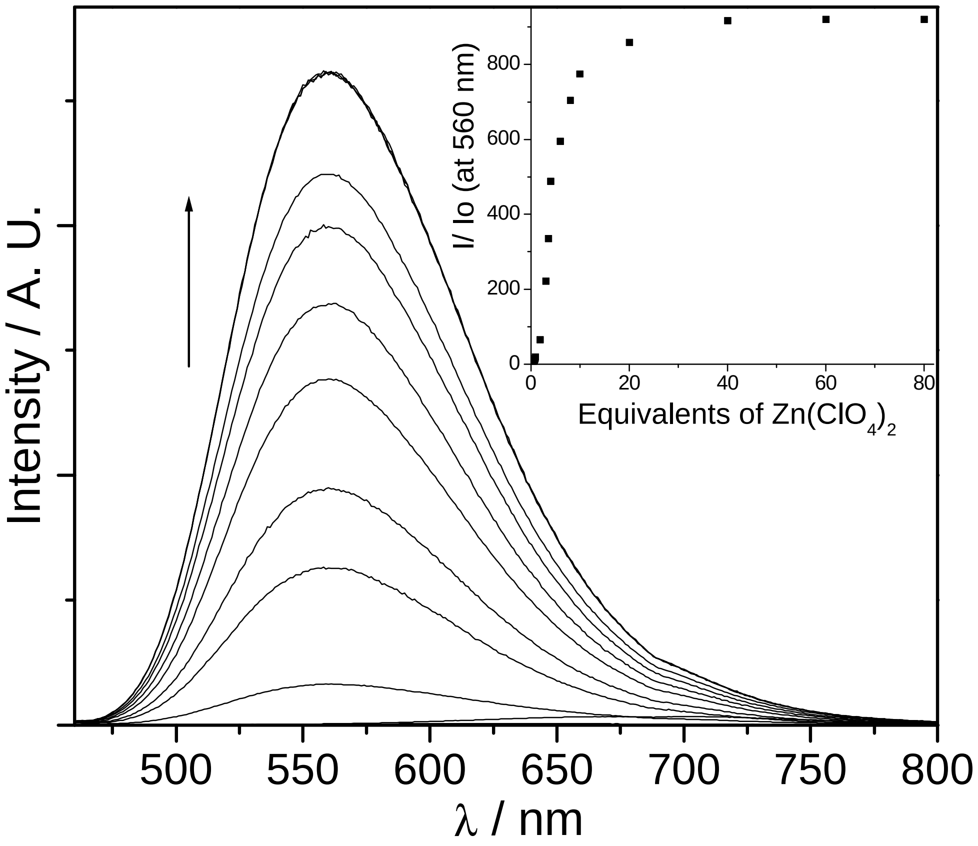


Figure S2. Emission spectral traces and (inset) luminescence enhancement factor (≡ I/I_o; monitored at 563 nm) of **1** at increasing equivalents of $Ca(ClO_4)_2$ in 0.1 M *n*Bu_4NPF_6 acetonitrile solution at 298 K (λ_{ex} = 405 nm, [**1**] = 3.2×10^{-5} mol dm^{-3}).

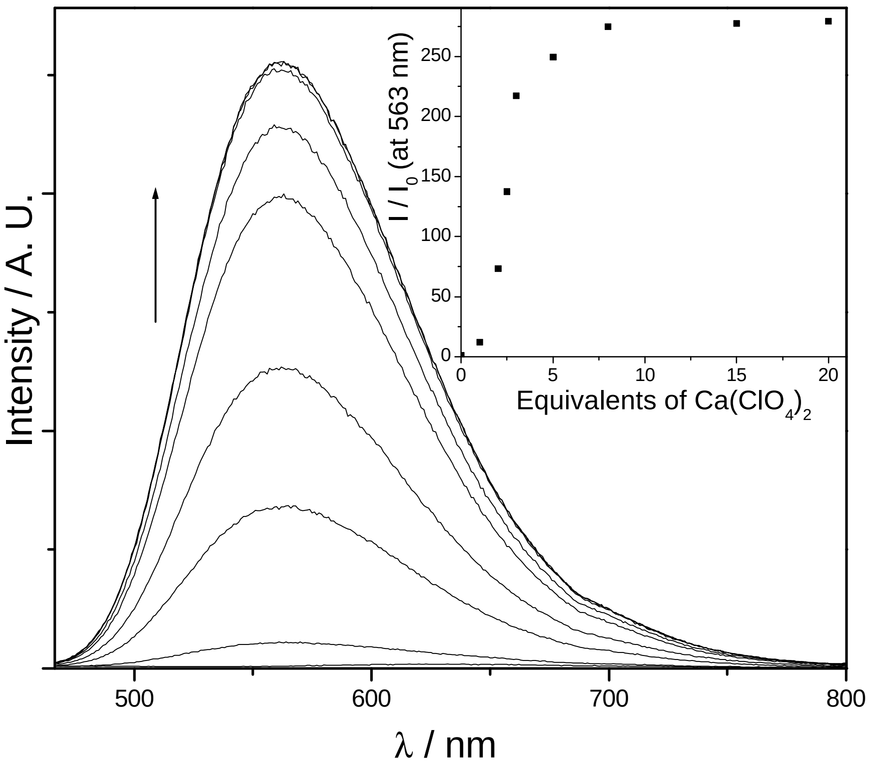


Figure S3. Emission spectral traces and (inset) luminescence enhancement factor (≡ I/I_o; monitored at 600 nm) of **1** at increasing equivalents of $NaClO_4$ in 0.1 M $n$$Bu_4NPF_6$ acetonitrile solution at 298 K (λ_{ex} = 405 nm, [**1**] = 3.2×10^{-5} mol dm^{-3}).

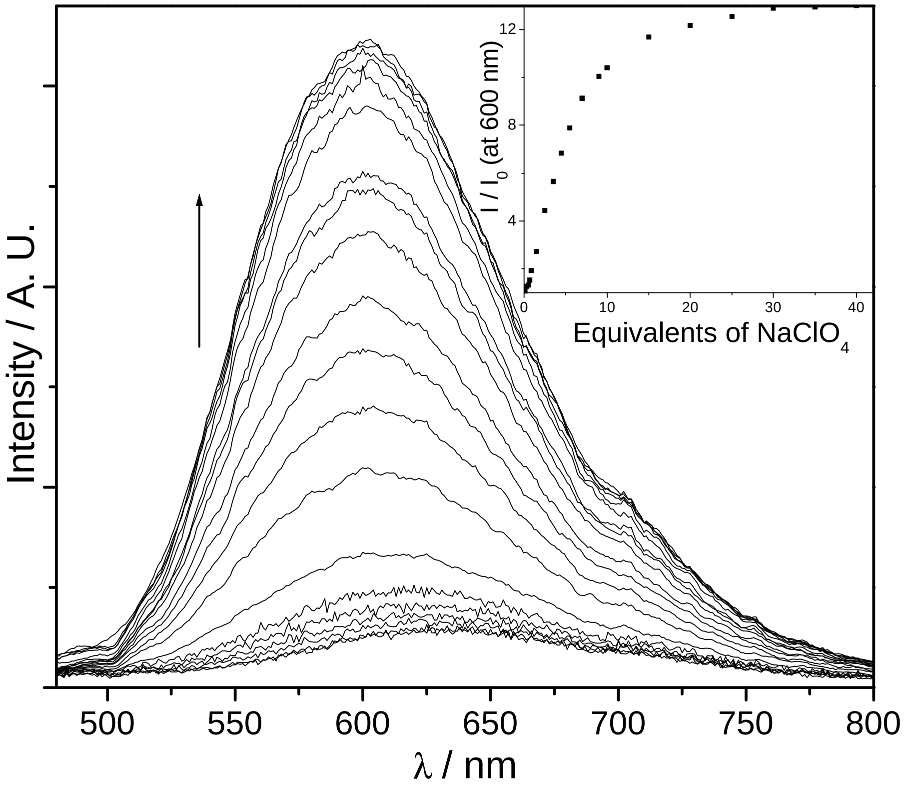
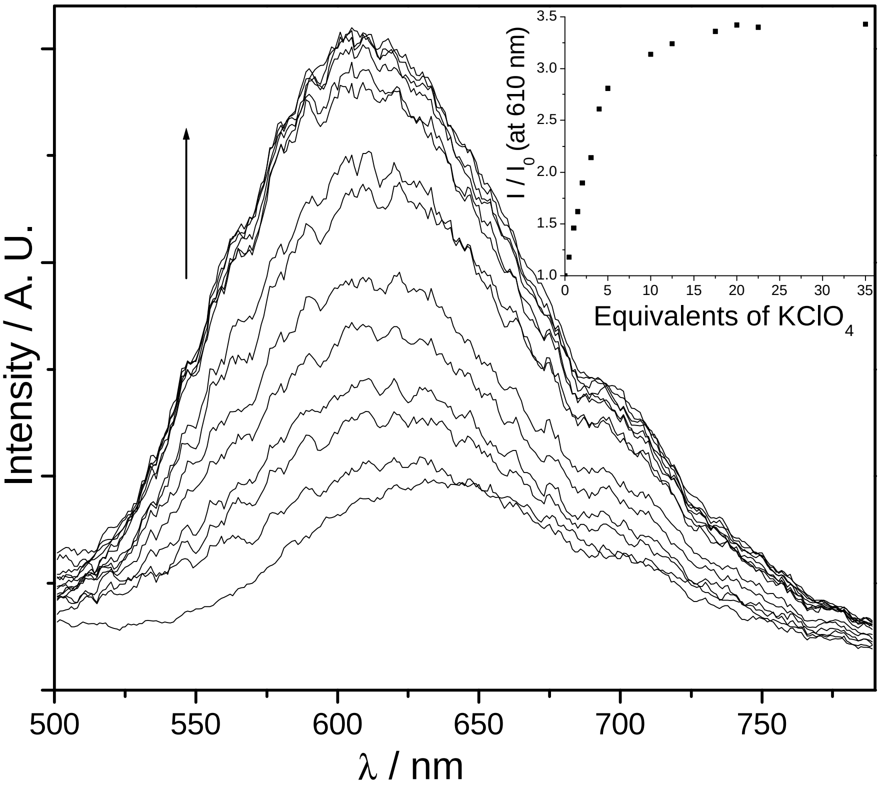


Figure S4. Emission spectral traces and (inset) luminescence enhancement factor (≡ I/I_o; monitored at 610 nm) of **1** at increasing equivalents of $KClO_4$ in 0.1 M *n*Bu_4NPF_6 acetonitrile solution at 298 K (λ_{ex} = 405 nm, [**1**] = 3.2×10^{-5} mol dm^{-3}).



Study of Binding of [Pt(*t*Bu$_2$bpy)(4-ethynylbenzo-15-crown-5)$_2$] (Pt) with M(ClO$_4$)$_x$ (M^{x+})

(A) The Binding Model

The binding of a platinum complex (Pt) with ions M^{x+} can be described by the following equilibria:

$$\begin{array}{rcll}
\mathrm{Pt} + \mathrm{M}^{x+} & \rightleftharpoons & \mathrm{PtM}^{x+} & K_{11} \\
\mathrm{PtM}^{x+} + \mathrm{M}^{x+} & \rightleftharpoons & \mathrm{Pt(M}^{x+})_2 & K_{12} \\
\mathrm{Pt(M}^{x+})_2 + \mathrm{M}^{x+} & \rightleftharpoons & \mathrm{Pt(M}^{x+})_3 & K_{13} \\
\vdots & & \vdots & \vdots \\
\mathrm{Pt(M}^{x+})_{n-1} + \mathrm{M}^{x+} & \rightleftharpoons & \mathrm{Pt(M}^{x+})_n & K_{1n}
\end{array}$$

The following symbols are used:

Pt(t): total concentration of species containing platinum complex, which is constant during the titration.

M^{x+}(t): total concentration of species containing M^{x+}.

[Pt]: platinum complex concentration at equilibrium.

[M^{x+}]: concentration of M^{x+} at equilibrium.

[Pt(M^{x+})$_n$]: equilibrium concentration of Pt(M^{x+})$_n$ species, n = 1, 2, 3, …

K_{1n}: stepwise equilibrium constants as illustrated in the above reaction scheme, n = 1, 2, 3, …

I: emission intensity during titration.

I_0: initial emission intensity, without adding any M^{x+}.

$$I = k_0[\mathrm{Pt}] + k_1[\mathrm{PtM}^{x+}] + k_2[\mathrm{Pt(M}^{x+})_2] + k_3[\mathrm{Pt(M}^{x+})_3] + ... + k_n[\mathrm{Pt(M}^{x+})_n],$$

where k_n (n = 1, 2, 3, …) are constant related to the extinction coefficient of the species and the intensity of excitation radiation (D. A. Skoog, J. J. Leary, *Principles of Instrumental Analysis*, 4th ed., Saunders College Publishers, **1992**).

$$\begin{aligned}
I &= k_0[\mathrm{Pt}] + k_1K_{11}[\mathrm{Pt}][\mathrm{M}^{x+}] + k_2K_{11}K_{12}[\mathrm{Pt}][\mathrm{M}^{x+}]^2 + k_3K_{11}K_{12}K_{13}[\mathrm{Pt}][\mathrm{M}^{x+}]^3 + ... + \\
&\quad k_nK_{11}K_{12}K_{13}...K_{1n}[\mathrm{Pt}][\mathrm{M}^{x+}]^n \\
&= [\mathrm{Pt}]\{k_0 + k_1K_{11}[\mathrm{M}^{x+}] + k_2K_{11}K_{12}[\mathrm{M}^{x+}]^2 + k_3K_{11}K_{12}K_{13}[\mathrm{M}^{x+}]^3 + ... + \\
&\quad k_nK_{11}K_{12}K_{13}...K_{1n}[\mathrm{M}^{x+}]^n\} \qquad \text{(i)}
\end{aligned}$$

$$I_0 = k_0[Pt(t)], \text{ by definition} \tag{ii}$$

$$\begin{aligned}[Pt(t)] &= [Pt] + [PtM^{x+}] + [Pt(M^{x+})_2] + [Pt(M^{x+})_3] + ... + [Pt(M^{x+})_n] \\ &= [Pt]\{1 + K_{11}[M^{x+}] + K_{11}K_{12}[M^{x+}]^2 + K_{11}K_{12}K_{13}[M^{x+}]^3 + \\ &\quad ... + K_{11}K_{12}K_{13}...K_{1n}[M^{x+}]^n\}\end{aligned} \tag{iii}$$

Substitute equation (iii) into (ii), which in turn substitute into (i) and rearrange, the following equation is obtained.

$$\begin{aligned}I - I_0 = [Pt]\{&(k_1 - k_0)K_{11}[M^{x+}] + (k_2 - k_0)K_{11}K_{12}[M^{x+}]^2 + (k_3 - k_0)K_{11}K_{12}K_{13}[M^{x+}]^3 + \\ &... + (k_n - k_0)K_{11}K_{12}K_{13}...K_{1n}[M^{x+}]^n\}\end{aligned} \tag{iv}$$

Eliminating the [Pt] terms by combining equations (iii) and (iv),

$$\begin{aligned}I - I_0 = [Pt(t)]\{&(k_1 - k_0)K_{11}[M^{x+}] + (k_2 - k_0)K_{11}K_{12}[M^{x+}]^2 + (k_3 - k_0)K_{11}K_{12}K_{13}[M^{x+}]^3 \\ &+ ... + (k_n - k_0)K_{11}K_{12}K_{13}...K_{1n}[M^{x+}]^n\} / \{1 + K_{11}[M^{x+}] + K_{11}K_{12}[M^{x+}]^2 + \\ &K_{11}K_{12}K_{13}[M^{x+}]^3 + ... + K_{11}K_{12}K_{13}...K_{1n}[M^{x+}]^n\}\end{aligned} \tag{v}$$

During the whole experiment, the concentration of M^{x+} is in large excess when compared with the concentration of Pt, hence we can use the following approximation,

$$[M^{x+}] \approx [M^{x+}(t)]$$

Therefore, equation (v) becomes,

$$\begin{aligned}I - I_0 = [Pt(t)]\{&(k_1 - k_0)K_{11}[M^{x+}(t)] + (k_2 - k_0)K_{11}K_{12}[M^{x+}(t)]^2 + (k_3 \\ &- k_0)K_{11}K_{12}K_{13}[M^{x+}(t)]^3 + ... +(k_n - k_0)K_{11}K_{12}K_{13}...K_{1n}[M^{x+}(t)]^n\} / \{1 + \\ &K_{11}[M^{x+}(t)] + K_{11}K_{12}[M^{x+}(t)]^2 + K_{11}K_{12}K_{13}[M^{x+}(t)]^3 + \\ &... + K_{11}K_{12}K_{13}...K_{1n}[M^{x+}(t)]^n\}\end{aligned} \tag{vi}$$

Equation (vi) is the general equation used in our study. The cases for n = 1, 2, 3, ... are therefore obtained.

Case 1: n = 1

Using equation (vi) up to the first term, and employing the following symbols to simplify the equation,

$\theta_1 = K_{11}$

$\theta_2 = k_1 - k_0$

$$I = \theta_1\theta_2[Pt(t)][M^{x+}(t)] / (1 + \theta_1[M^{x+}(t)]) + I_0 \qquad (1)$$

Case 2: n = 2

Using equation (vi) up to the second term, and employing the following symbols to simplify the equation,

$\theta_1 = K_{11}$

$\theta_2 = K_{12}$

$\theta_3 = k_1 - k_0$

$\theta_4 = k_2 - k_0$

$$I = [Pt(t)][M^{x+}(t)]\theta_1(\theta_3 + \theta_2\theta_4[M^{x+}(t)]) / (1 + \theta_1[M^{x+}(t)] + \theta_1\theta_2[M^{x+}(t)]^2) + I_0 \qquad (2)$$

Case 3: n = 3

Using equation (vi) up to the third term, and employing the following symbols to simplify the equation,

$\theta_1 = K_{11}$

$\theta_2 = K_{12}$

$\theta_3 = K_{13}$

$\theta_4 = k_1 - k_0$

$\theta_5 = k_2 - k_0$

$\theta_6 = k_3 - k_0$

$$I = [Pt(t)][M^{x+}(t)]\theta_1\{\theta_4 + \theta_2[M^{x+}(t)](\theta_5 + \theta_6\theta_3[M^{x+}(t)])\} / 1 + \theta_1[M^{x+}(t)]\{1 + \theta_2[M^{x+}(t)](1 + \theta_3[M^{x+}(t)])\} + I_0 \qquad (3)$$

As equation (3) would involve six fitting parameters, this would require a large number of experimental data for meaningful fitting; some assumptions may be applied to decrease the number of fitting parameters. A possible assumption is $k_1 = k_2 = k_3$. Therefore equation (3) can be simplified into equation (3’).

$$I = [Pt(t)][M^{x+}(t)]\theta_1\theta_4\{1 + \theta_2[M^{x+}(t)](1 + \theta_3[M^{x+}(t)])\} / 1 + \theta_1[M^{x+}(t)]\{1 + \theta_2[M^{x+}(t)](1 + \theta_3[M^{x+}(t)])\} + I_0 \qquad (3')$$

Where $\theta_4 = k_1 - k_0 = k_2 - k_0 = k_3 - k_0$

Other cases: n ³ 4

Similar equations can be derived. When n increases by one, it results in two more fitting parameters. This becomes impractical to collect a large number of experimental data required for a meaningful fitting.

The non linear fits were performed by inputting the experimental data into the specific models using least squares method (K. Levenberg, *Q. Appl. Math.* **1944**, *2*, 164–168; an algorithm for least-squares estimation of nonlinear parameters: D. Marquardt, *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431–441). The DRNLIN subroutine of the IMSL STAT/LIBRARY (IMSL STAT/LIBRARY: Houston, Texas, Visual Numerics, Inc., **1999**) was used. A main Fortran 90 program was employed to perform the input and output of the data and parameters setting for the DRNLIN subroutine. They were compiled and linked by a Digital Visual Fortran 5.0 compiler and the executive was run on a Pentium III type PC under Window 2000 Professional.

(B) Fitting the experimental emission data as a function of $[M(ClO_4)_x]$

Table 2 Result on the fitting of equilibrium expressions for binding Na^+, Mg^{2+} and Zn^{2+} to **1**.

Ion	**n**	K_{11}	K_{12}	K_{13}	b
Na^+	2	7.27×10^3	1.08×10^4		7.9×10^7
	3	3.35×10^3	5.56×10^3	9.97×10^2	1.9×10^{10}
Mg^{2+}	2	3.11×10^3	1.69×10^5		5.3×10^8
	3	1.43×10^1	1.93×10^7	5.94×10^4	1.6×10^{13}
Zn^{2+}	2	2.11×10^3	4.41×10^4		9.3×10^7
	3	3.38×10^4	4.48×10^3	2.69×10^4	4.1×10^{12}

β is the overall equilibrium constant = $\prod^n K_{1n}$

Table 3 Summary of Hill Plot

Ion	**n**	b
Na^+	1.7	6.5×10^6
Mg^{2+}	2.2	3.7×10^9
Zn^{2+}	2.0	5.5×10^7

The data of these three ions can both give well fitted curves for the n = 2 and n = 3 equations. When we compare the overall equilibrium constants (β), obtained in the nonlinear least-squares fits (Table 2) with that from Hill plot (Table 3), all the n = 3 cases give unreasonably large values of β in Table 2. The mathematically explanation for this can be: since the equation for n = 3 contains more fitting parameters than that for n = 2, any set of data fits the n = 2 equation well is also expected to fit the n = 3 case well. This is called the over-fitted phenomenon. In this case, the β values obtained for n = 3 in Table 2 are physically absurd. Therefore, we can rule out all the n = 3 cases.

For n = 2, in the case of Na^+, the value of K_{12} is comparable to that of K_{11}. In the case of Zn^{2+}, the K_{12} value is about 20 times larger than that of K_{11}. In the case of Mg^{2+}, the K_{12} value is more than 50 times larger than K_{11}. All β values in the case of n = 2 are consistent with those found in Hill plot.

Conclusion

In this present study, the fittings of emission intensity enhanced by Na^+, Mg^{2+} and Zn^{2+} ions give equilibrium constants that are consistent with those obtained from Hill plots and the stepwise equilibrium constants can also be accurately determined.