

A Heterobimetallic Ru(II)-Cu(II) Donor-Acceptor Complex as a Chemodosimetric Ensemble for Selective Cyanide Detection

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Supporting Information

Fig. 1 IR spectra of **1** with KBr pellet. The $\nu_{\text{C}\equiv\text{N}}$ (cm^{-1}) of **1** is located at 2055 cm^{-1} .

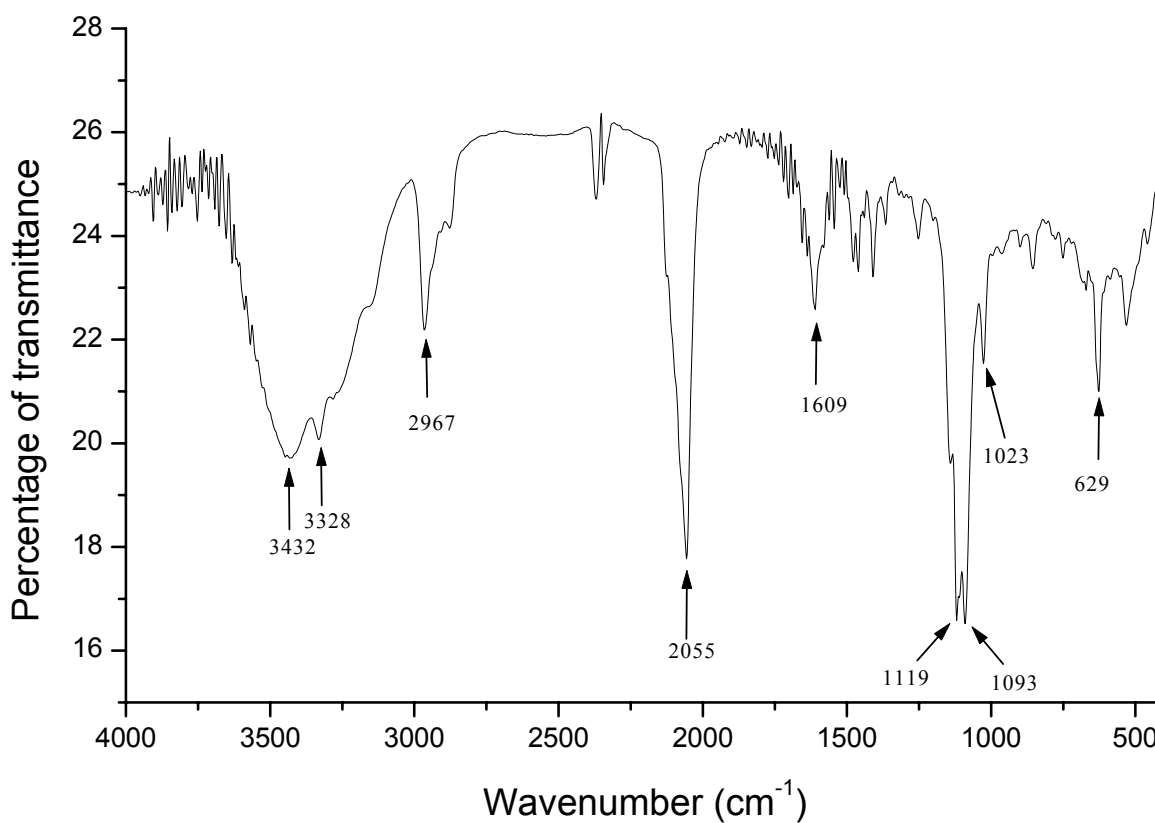


Fig. 2 Solution IR spectrum of 1 in methanol.

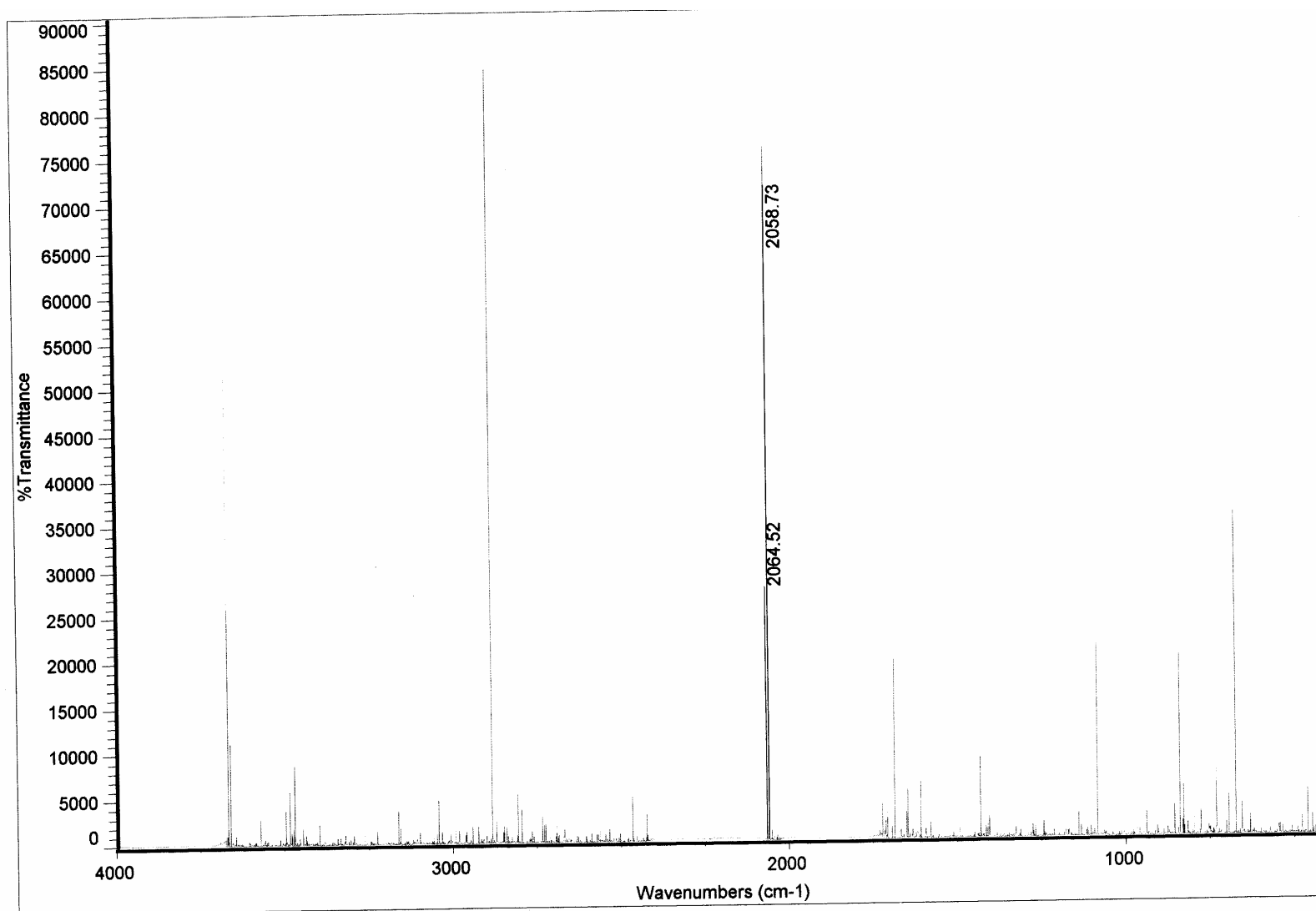


Fig. 3 Isotopic distribution of ESI-MS of $\{\text{Ru}^{\text{II}}(\text{tBubpy})(\text{CN})_4\text{-}[\text{Cu}^{\text{II}}(\text{dien})]_2\}^{2+}$ (**1**) in methanol. The parent ion at m/z 907 corresponds to $[\text{M} - \text{ClO}_4]^+$ fragment. The simulated isotopic distribution is shown in the inset.

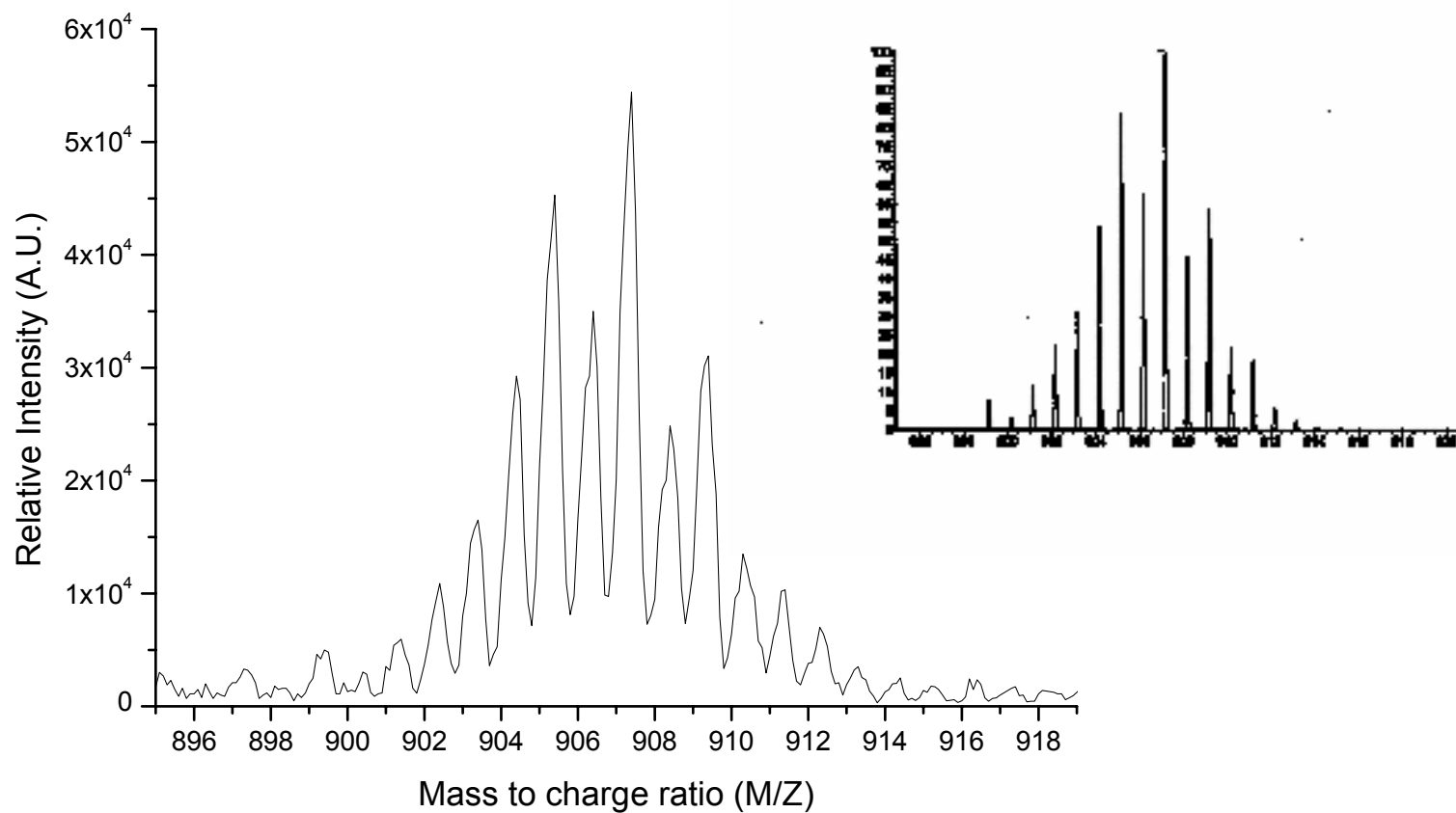


Fig. 4 Binding isotherm of *cis*-[Ru(bpy)₂(CN)₂] (1.25×10^{-3} M in 1:1 DMF:HEPES) by [Cu(dien)](ClO₄)₂ monitored by the quenching of the ³MLCT emission of *cis*-[Ru(bpy)₂(CN)₂] at 634 nm. The binding equilibrium is reached at 1:1 *cis*-[Ru(bpy)₂(CN)₂]:[Cu(dien)](ClO₄)₂. Thus, the donor-acceptor adduct, **2**, formed is denoted *cis*-[Ru(bpy)₂(CN)₂]-[Cu(dien)]²⁺.

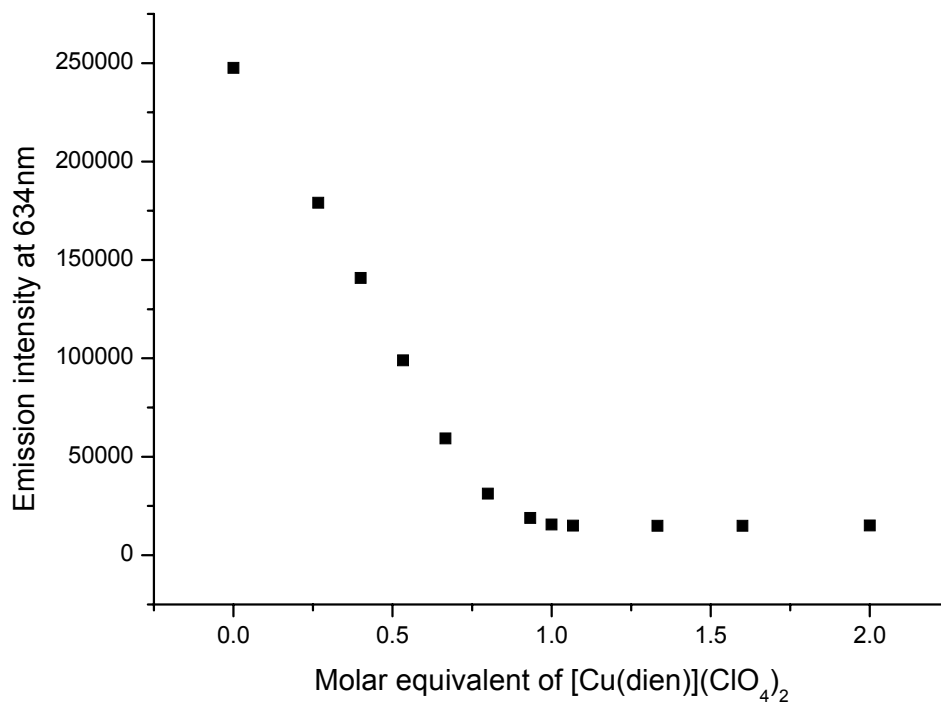


Fig. 5 Spectrofluorimetric titration of *cis*-[Ru(bpy)₂(CN)₂] (5.0×10^{-5} M) with [Cu(dien)](ClO₄)₂ (0 to 2.0×10^{-3} M) in aqueous DMF (1:1 v/v) (pH 7.4). The slope and y-intercept of the best fitted $I_0/(I-I_0)$ vs. $1/[Cu(dien)]^{2+}$ plot are $2.14 \pm 0.052 \times 10^{-3}$ M and $8.97 \pm 0.67 \times 10^{-1}$ respectively. According to Equation (2), the ΔG° of formation of the donor-acceptor adduct **2** is estimated to be -14.8 kJ mol⁻¹.

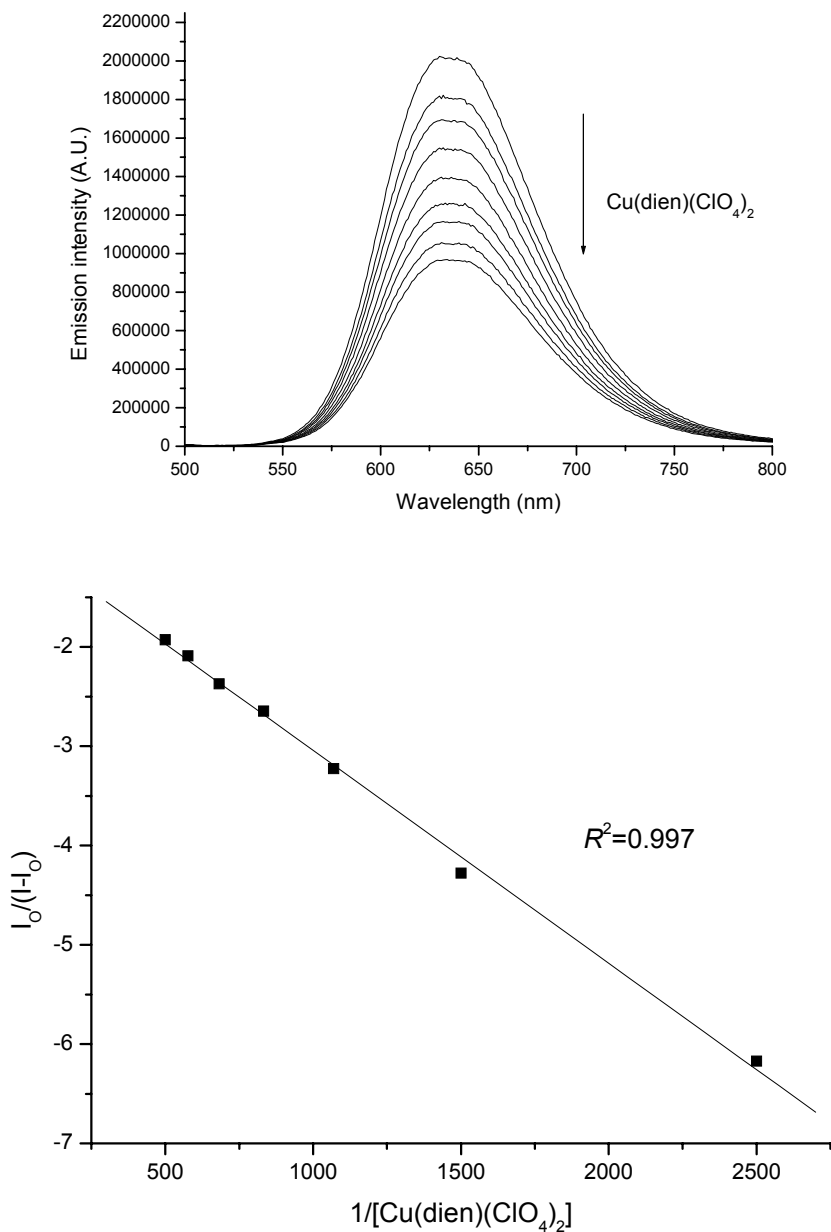


Fig 6 Isotopic distribution of ESI-MS of the m/z 497 peak corresponding to $[\text{Ru}(\text{Bubpy})(\text{CN})_4 + \text{Na}]^-$ obtained from a mixture of **1** and sodium cyanide. The simulated isotopic distribution is shown in the inset.

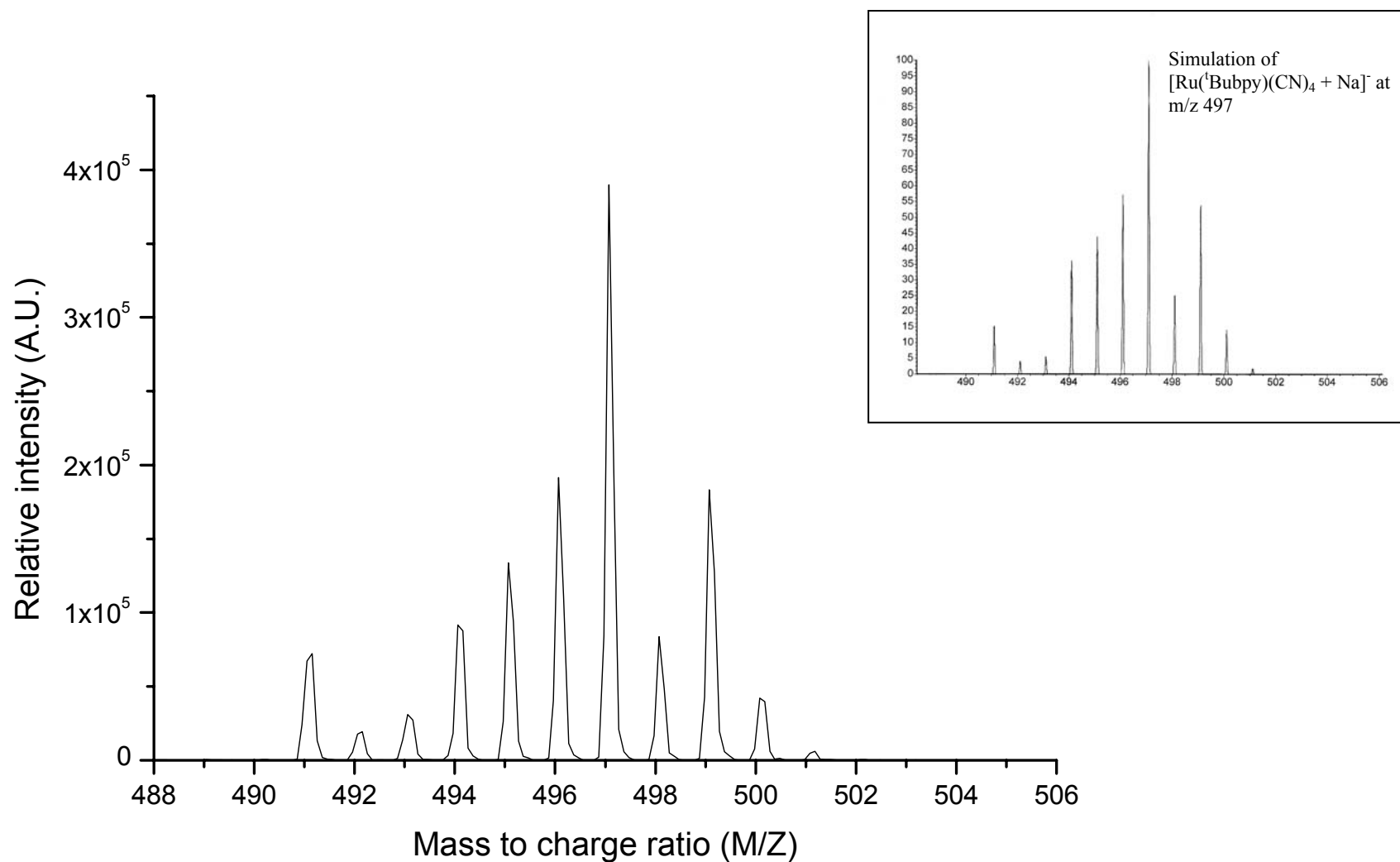


Fig. 7 Job's plot of the luminescent responses of solvated **1** (L = solvent) towards cyanide showing that the maximum response occurs at 1:CN⁻ mole ratio of 1:4. This implies that each Cu(II) center of **1** binds two CN⁻.

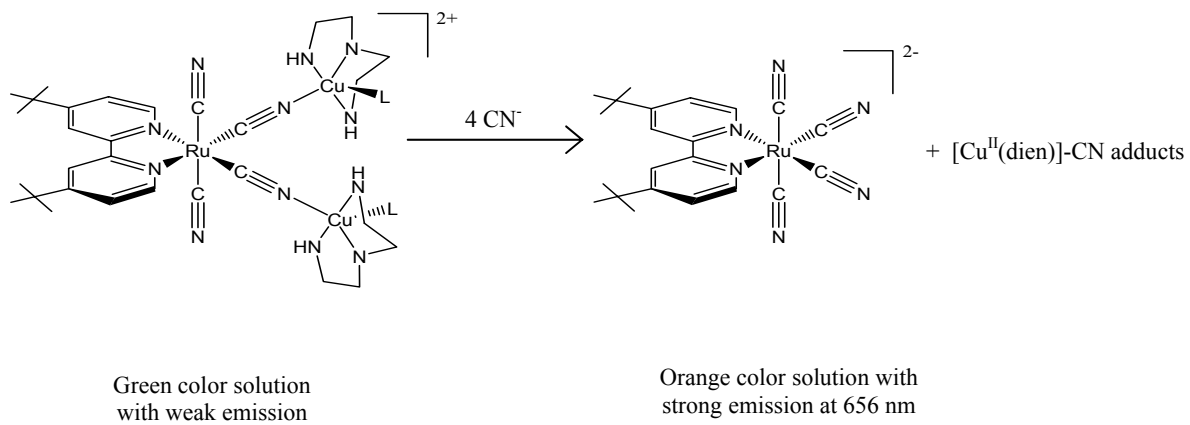
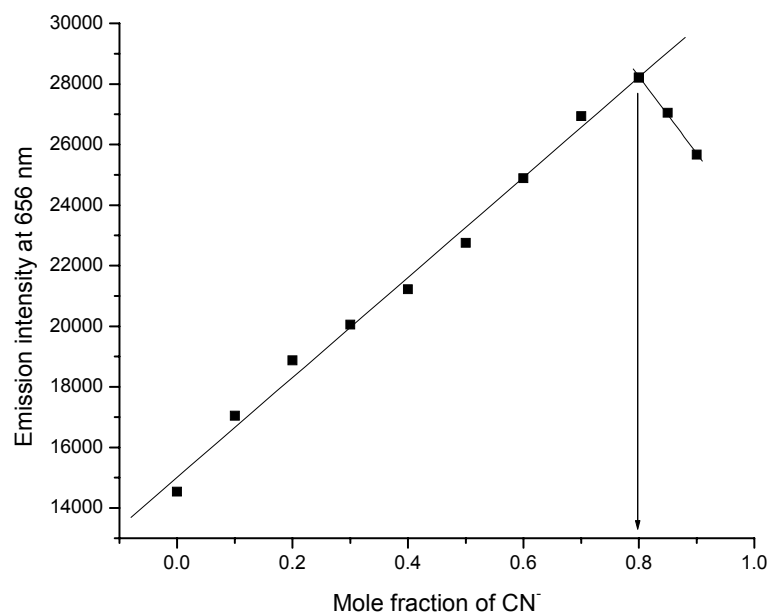


Fig. 8 Fitting of the luminescent responses $I_0/(I-I_0)$ of **1** ($1.40 \times 10^{-4} M$) at 656 nm towards CN^- according to the 1:2 binding model. The slope and y-intercept of the best fitted $I_0/(I-I_0)$ vs. $1/[CN^-]^2$ plot are $7.94 \pm 0.069 \times 10^{-9} M^2$ and $5.87 \pm 0.11 \times 10^{-2}$ respectively. The luminescent responses of **1** are shown in the inset.

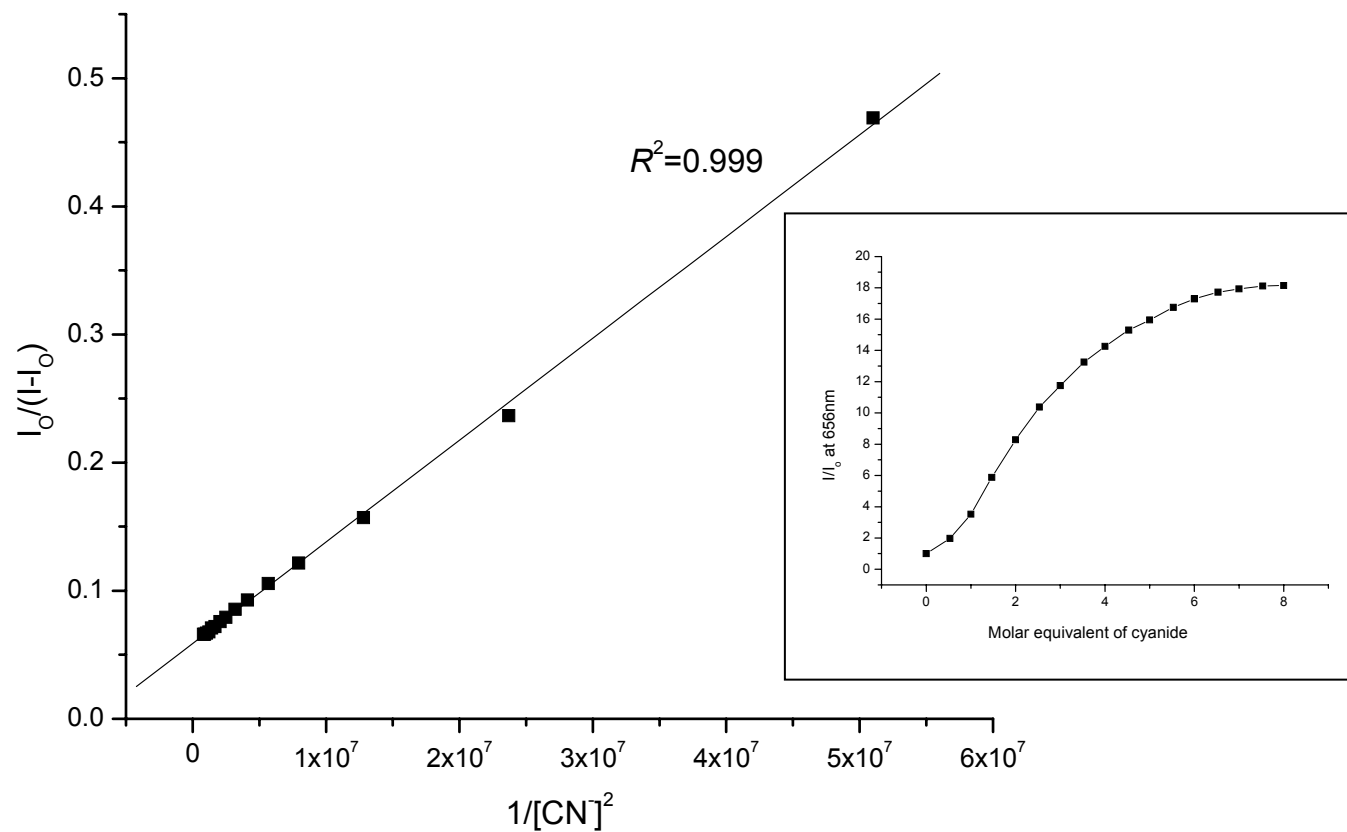


Fig. 9 Summary of UV-vis spectroscopic (top left) and spectrofluorimetric (top right) titrations of **1** (1.40×10^{-4} M) by common anions monitored as a function of the increase in absorbance (A/A_0 at 475 nm) and emission (I/I_0 at 656 nm) respectively. All titrations were carried out in aqueous DMF (1:1 v/v) at pH 7 at 298 K.

