Electronic Supplementary Material (ESI) for Dalton Transactions. This journal is © The Royal Society of Chemistry 2015

Supporting Information

A phthalazine-based two-in-one chromogenic receptor for detecting Co²⁺ and Cu²⁺ in aqueous environment

Jae Jun Lee, Ye Won Choi, Ga Rim You, Sun Young Lee, Cheal Kim*

Department of Fine Chemistry and Department of Interdisciplinary Bio IT Materials, Seoul National University of Science and Technology, Seoul 139-743, Korea. Fax: +82-2-973-9149; Tel: +82-2-970-6693; E-mail: <u>chealkim@seoultech.ac.kr</u>

The method of determination of association constant (*K*). Based on the literatures,^{1,2} the association constant (*K*) of sensor 1 (L) with Co^{2+} or Cu^{2+} (M) can be expressed by the following equations, where (L) and (M) are assumed to form a complex with a complexation ratio of m:n.

$$[M]^{m} = \frac{1}{nK_{[L]}^{n-1}} \frac{1-\alpha}{\alpha^{n}}, \quad \alpha = \frac{[L]}{[L]_{T}}$$

 α is defined as the ratio between the free ligand concentration [L] and the initial concentration of ligand [L]_T.

References

[1] G. Grynkiewicz, M. Poenie, R. Y. Tsien, J. Biol. Chem., 1985, 260, 3440.

[2] C.-Y. Li, X.-B. Zhang, Y.-Y. Dong, Q.-J. Ma, Z.-X. Han, Y. Zhao, G.-L. Shen, R.-Q. Yu, *Anal. Chim. Acta*, 2008, **616**, 214.



Fig. S1. (a) Fluorescence spectra of 1 (10 μ M, λ_{ex} = 370 nm) upon addition of various anions (30 equiv) in bis-tris buffer (10 mM bis-tris, pH = 7.0). (b) Bar graph representing the change

(a)

of the relative emission intensity of 1 (10 µM) at 480 nm upon treatment with various anions



Fig. S2. Job plot for the binding of **1** with Co^{2+} Absorbance at 512 nm was plotted as a function of the molar ratio of $[Co^{2+}]/([1]+[Co^{2+}])$. The total concentration of Co^{2+} ions with receptor **1** was 2.0 x 10⁻⁵ M.



Fig. S3. Absorption spectra and color changes of 1 (10 μ M) with Co²⁺ under the degassed and oxygenous conditions.



Fig. S4. ¹H NMR titration of 1 with Co²⁺.



Fig. S5. Li's equation plot (absorbance at 512 nm) of 1, assuming 2:1 stoichiometry for association between 1 and Co²⁺. 'Ct' means the concentration of 1, and 'a' does $[(A_x - A_{max})/(A_0 - A_{max})]$.



Fig. S6. Detection limit based on change in the ratio (absorbance at 512 nm) of 1 (10 μ M) with Co²⁺. DL indicates a detection limit based on the 3 σ /slop.



Fig. S7. Bar graph representing the changes of the absorbance (512 nm) of 1 (10 μ M) with Co²⁺ (0.5 equiv) in the absence and presence of 0.5 equiv of various metal ions in bis-tris buffer.



Fig. S8. Job plot for the binding of **1** with Cu^{2+} Absorbance at 420 nm was plotted as a function of the molar ratio of $[Cu^{2+}]/([1]+[Cu^{2+}])$. The total concentration of Cu^{2+} ions with receptor **1** was 2.0 x 10⁻⁵ M.



Fig. S9. Li's equation plot (absorbance at 472 nm) of 1, assuming 2:1 stoichiometry for association between 1 and Cu²⁺. 'Ct' means the concentration of 1, and 'a' does $[(A_x - A_{max})/(A_0 - A_{max})]$.



Fig. S10. Detection limit based on change in the ratio (absorbance at 472 nm) of 1 (10 μ M) with Cu²⁺. DL indicates a detection limit based on the 3 σ /slop.



Fig. S11. Bar graph representing the changes of the absorbance (472 nm) of 1 (10 μ M) with Cu²⁺ (0.5 equiv) in the absence and presence of 0.5 equiv of various metal ions in bis-tris buffer.



Fig. S12. Absorbance (at 512 nm) of **1** as a function of Co(II) concentration. $[1] = 30 \,\mu\text{mol/L}$ and $[Co(II)] = 0.00-6.00 \,\mu\text{mol/L}$ in buffer-DMSO solution (999:1, 10 mM bis-tris, pH 7.0).



Fig. S13. Absorbance (at 512 nm) of **1** as a function of Cu(II) concentration. $[1] = 30 \,\mu\text{mol/L}$ and $[Cu(II)] = 0.00-6.00 \,\mu\text{mol/L}$ in buffer-DMSO solution (999:1, 10 mM bis-tris, pH 7.0).



(b)



(a)



(c)

Fig. S14. The energy-minimized structures of (a) 1, (b) $Co^{3+}-2\cdot 1$ and (c) $Cu^{2+}-2\cdot 1$.



(a)

(b)

Excited State 1	Wavelength	Percent (%)	Oscillator strength
$H \rightarrow L$	381.48 nm	98%	0.9468
Excited State 10	Wavelength	Percent (%)	Oscillator strength
$H \rightarrow L+3$	274.11 nm	69%	0.357
$H-3 \rightarrow L$		15%	
$H-1 \rightarrow L+1$		9%	
Excited State 11	Wavelength	Percent (%)	Oscillator strength
$H-1 \rightarrow L+1$	266.58 nm	71%	0.1602
$H-5 \rightarrow L$		14%	
$H-3 \rightarrow L$		4%	
$H \rightarrow L+3$		3%	

Fig. S15. (a) The theoretical excitation energies and the experimental UV-vis spectrum of 1. (b) The major electronic transition energies and molecular orbital contributions for 1 (H = HOMO and L = LUMO).



Fig. S16. Isosurface (0.030 electron bohr⁻³) of molecular orbitals participating in the major singlet excited states of **1**.



(b	I)

Excited State 15	Wavelength	Percent (%)	Main character	Oscillator strength
$H \rightarrow L+2$	502.63 nm	30%	LMCT	0.2314
$H-1 \rightarrow L$		26%	ICT	
$H-1 \rightarrow L+3$		22%	LMCT	
$H \rightarrow L+1$		18%	ICT, LMCT	
Excited State 16	Wavelength	Percent (%)	Main character	Oscillator strength
				0
$H-1 \rightarrow L+1$	494.51 nm	70%	ICT	0.3557
$\begin{array}{c} \text{H-1} \rightarrow \text{L+1} \\ \text{H-1} \rightarrow \text{L+2} \end{array}$	494.51 nm	70% 14%	ICT LMCT	0.3557
$\begin{array}{c} \mathrm{H}\text{-}\mathrm{l} \rightarrow \mathrm{L}\text{+}\mathrm{l} \\ \mathrm{H}\text{-}\mathrm{l} \rightarrow \mathrm{L}\text{+}\mathrm{2} \\ \mathrm{H} \rightarrow \mathrm{L} \end{array}$	494.51 nm	70% 14% 12%	ICT LMCT ICT	0.3557
$H-1 \rightarrow L+1$ $H-1 \rightarrow L+2$ $H \rightarrow L$ Excited State 22	494.51 nm Wavelength	70% 14% 12% Percent (%)	ICT LMCT ICT Main character	0.3557 Oscillator strength
$H-1 \rightarrow L+1$ $H-1 \rightarrow L+2$ $H \rightarrow L$ Excited State 22 $H-1 \rightarrow L+3$	494.51 nm Wavelength 469.61 nm	70% 14% 12% Percent (%) 62%	ICT LMCT ICT Main character LMCT	0.3557 Oscillator strength 0.1762

(a)

$H \rightarrow L+1$	4%	ICT, LMCT
$H \rightarrow L+2$	4%	LMCT

Fig. S17. (a) The theoretical excitation energies and the experimental UV-vis spectrum of $Co^{3+}-2\cdot 1$. (b) The major electronic transition energies and molecular orbital contributions for $Co^{3+}-2\cdot 1$ (H = HOMO and L = LUMO).



Fig. S18. Isosurface (0.030 electron bohr⁻³) of molecular orbitals participating in the major singlet excited states of $Co^{3+}-2\cdot 1$.



(b)

Excited State 13	Wavelength	Percent (%)	Main character	Oscillator strength
H-1 (α) \rightarrow L+1 (α)	492.02 nm	28%	ICT	0.3536
$\mathrm{H}\left(\alpha\right)\to\mathrm{L}\left(\alpha\right)$		7%	ICT	
H-1 (β) \rightarrow L+2 (β)		30%	ICT	
H-7 (β) \rightarrow L (β)		15%	LMCT, d-d	
$\mathrm{H}\left(\beta\right) \to \mathrm{L+1}\left(\beta\right)$		8%	ICT	
H-2 $(\beta) \rightarrow L(\beta)$		4%	LMCT, d-d	
$\mathbf{T} = \mathbf{T} = $		20/		
$H-24 (\beta) \rightarrow L (\beta)$		3%	LMCT, d-d	
$\frac{\text{H-24 } (\beta) \rightarrow \text{L} (\beta)}{\text{Excited State 14}}$	Wavelength	3% Percent (%)	LMCT, d-d Main character	Oscillator strength
$\frac{\text{H-24 } (\beta) \rightarrow \text{L } (\beta)}{\text{Excited State 14}}$ $\frac{\text{H-1 } (\alpha) \rightarrow \text{L } (\alpha)}{\text{H-1 } (\alpha) \rightarrow \text{L } (\alpha)}$	Wavelength 483.05 nm	3% Percent (%) 30%	IMC1, d-d Main character ICT	Oscillator strength 0.5575
$\frac{\text{H-24 } (\beta) \rightarrow \text{L } (\beta)}{\text{Excited State 14}}$ $\frac{\text{H-1 } (\alpha) \rightarrow \text{L } (\alpha)}{\text{H } (\alpha) \rightarrow \text{L+1 } (\alpha)}$	Wavelength 483.05 nm	3% Percent (%) 30% 13%	ICT ICT	Oscillator strength 0.5575
$ \begin{array}{c} \text{H-24 } (\beta) \rightarrow \text{L} (\beta) \\ \hline \textbf{Excited State 14} \\ \hline \text{H-1 } (\alpha) \rightarrow \text{L} (\alpha) \\ \text{H} (\alpha) \rightarrow \text{L+1} (\alpha) \\ \text{H-2 } (\alpha) \rightarrow \text{L} (\alpha) \end{array} $	Wavelength 483.05 nm	3% Percent (%) 30% 13% 2%	ICT ICT Main character	Oscillator strength 0.5575
$ \begin{array}{c} \text{H-24 } (\beta) \rightarrow \text{L} (\beta) \\ \hline \textbf{Excited State 14} \\ \hline \textbf{H-1} (\alpha) \rightarrow \text{L} (\alpha) \\ \text{H} (\alpha) \rightarrow \text{L+1} (\alpha) \\ \text{H-2} (\alpha) \rightarrow \text{L} (\alpha) \\ \hline \textbf{H-1} (\beta) \rightarrow \text{L+1} (\beta) \end{array} $	Wavelength 483.05 nm	3% Percent (%) 30% 13% 2% 31%	ICT ICT ICT MLCT ICT	Oscillator strength 0.5575
$\begin{array}{c} \text{H-24 } (\beta) \rightarrow \text{L} (\beta) \\ \hline \textbf{Excited State 14} \\ \hline \text{H-1 } (\alpha) \rightarrow \text{L} (\alpha) \\ \text{H} (\alpha) \rightarrow \text{L+1} (\alpha) \\ \text{H-2 } (\alpha) \rightarrow \text{L} (\alpha) \\ \hline \text{H-1 } (\beta) \rightarrow \text{L+1} (\beta) \\ \text{H} (\beta) \rightarrow \text{L+2} (\beta) \end{array}$	Wavelength 483.05 nm	3% Percent (%) 30% 13% 2% 31% 14%	ICT ICT ICT MLCT ICT ICT ICT	Oscillator strength 0.5575

H-25 (β) \rightarrow L (β)		2%	ICT	
Excited State 21	Wavelength	Percent (%)	Main character	Oscillator strength
H-2 (α) \rightarrow L+1 (α)	449.13 nm	18%	MLCT	0.2656
H-3 (α) \rightarrow L (α)		8%	MLCT	
H-1 (α) \rightarrow L+1 (α)		5%	ICT	
$\mathrm{H}\left(\alpha\right)\rightarrow\mathrm{L}\left(\alpha\right)$		3%	ICT	
H-7 (β) \rightarrow L (β)		34%	LMCT, d-d	
H-2 (β) \rightarrow L (β)		12%	LMCT, d-d	
H-1 (β) \rightarrow L+2 (β)		5%	ICT	
$\mathrm{H}\left(\beta\right) \to \mathrm{L+1}\left(\beta\right)$		3%	ICT	
H-2 (β) \rightarrow L+1 (β)		3%	MLCT	

Fig. S19. (a) The theoretical excitation energies and the experimental UV-vis spectrum of $Cu^{2+}-2\cdot 1$. (b) The major electronic transition energies and molecular orbital contributions for $Cu^{2+}-2\cdot 1$ (H = HOMO and L = LUMO / (α): α spin MO and (β): β spin MO).



Fig. S20. Isosurface (0.030 electron bohr⁻³) of molecular orbitals (α spin) participating in the major singlet excited states of Cu²⁺-2•1.



Fig. S21. Isosurface (0.030 electron bohr⁻³) of molecular orbitals (β spin) participating in the major singlet excited states of Cu²⁺-2•1.