

Phosphorescent Chemosensor Based on Iridium(III) Complex for the Selective Detection of Cu(II) Ion in Aqueous Acetonitrile

Hye-Bin Kim,[†] Yinan Li,[†] and Myung Ho Hyun^{†,‡,*}

[†]Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 690-735, Korea
*E-mail: mhhyun@pusan.ac.kr

[‡]Division of High Technology Materials Research, Busan Center, Korea Basic Science Institute (KBSI), Busan 618-230, Korea
Received October 8, 2012, Accepted November 20, 2012

Key Words : Iridium(III) complex, Phosphorescence quenching, Cu²⁺ detection, Phosphorescent chemosensor

Cu(II) ion has two sides. In one side, Cu(II) ion is an important cofactor in nearly 20 metalloenzymes and an essential micronutrient for all living systems.¹ But, in other side, Cu(II) ion is one of significant metal pollutants² and toxic to living cells if present in slightly high concentrations, causing neurodegenerative diseases such as Menkes and Wilson's disease.³ In this instance, the selective detection of Cu(II) ion in environment and in living systems is very important. Consequently, various fluorescent chemosensors for the highly sensitive and selective detection of Cu(II) ion have been developed.⁴

Phosphorescent chemosensors for the selective detection of Cu(II) ion are also attractive because long-lived phosphorescence can be discriminated readily from scattered light and short-lived background fluorescence normally present in biological samples.⁵ However, phosphorescent chemosensors for the selective detection of Cu(II) ion have been only sparingly reported. In phosphorescent chemosensors, heavy-metal complexes have been widely utilized as effective phosphors.⁶ Especially, cyclometalated iridium(III) complexes, which are known as efficient phosphorescent dopants in organic light emitting diodes (OLEDs),⁷ bonded to appropriate receptors have been utilized as phosphorescent chemosensors for the selective detection of Ca(II),⁸ Hg(II)⁹ or

fluoride ion.¹⁰ Very recently, an iridium(III) complex containing one 2-(2'-benzo[*b*]thienyl)pyridine (btp), two cyclometalating 2-phenylpyridine (ppy) ligands and a di(2-picolyl)amine (DPA) receptor tethered to the btp ligand by a methylene linker was reported to be an effective phosphorescent chemosensor for Cu(II) ion.¹¹

In this study, we wish to prepare another iridium(III) complex-based phosphorescent chemosensor for the selective detection of Cu(II) ion. Previously, iridium(III) complex containing 3,9-dithia-6-azaundecane receptor tethered to the 2,2'-bipyridine ligand was reported to be quite successful for the selective detection Hg(II) ion.¹² 3,9-Dithia-6-azaundecane receptor tethered to the 2,2'-bipyridine ligand in complex **1** has been proposed to be an effective receptor for Hg(II) ion.¹² Similarly, by replacing the 3,9-dithia-6-azaundecane receptor of the previously reported complex with a DPA receptor, which has been used as an effective receptor for Zn(II) or Cu(II) ion,^{4,14,13} the resulting complex **1** (Fig. 1) was expected to be a good phosphorescent chemosensor for the selective detection of Cu(II) ion.

Complex **1** was prepared as shown in Figure 1. By treating iridium(III) complex containing two cyclometalating 2-phenylpyridine (ppy) ligands and 4,4'-bis(bromomethyl)-2,2'-bipyridine, which was prepared according to the procedure

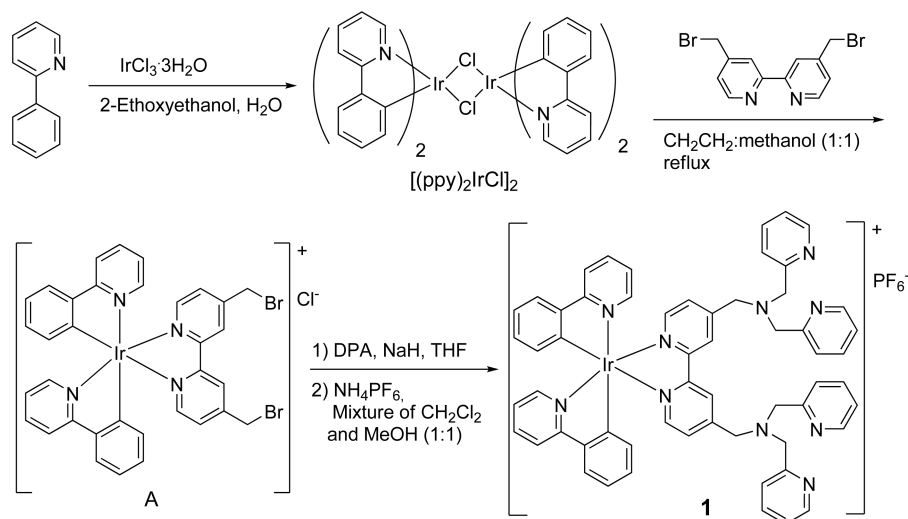


Figure 1. Scheme for the preparation of iridium(III) complex **1**.

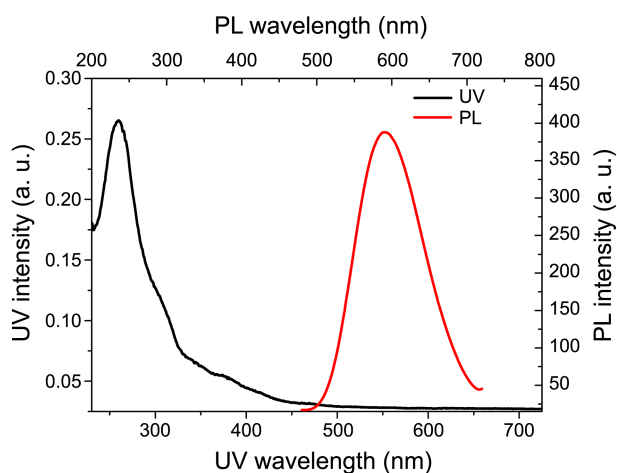


Figure 2. UV-Vis and phosphorescence spectra of iridium(III) complex **1** (10 μM) in 50% acetonitrile in water (excitation: 365 nm).

reported previously,¹² with DPA in the presence of NaH and then treating with NH_4PF_6 in the mixed solvent of methylene chloride and methanol (1:1, v/v), complex **1** was obtained.

Complex **1** showed the characteristic UV-Vis absorption and photoluminescence spectra in 50% acetonitrile in water. The intense absorption band at 250-290 nm in the UV-Vis spectrum of complex **1** shown in Figure 2 might be originated from the ligand-centered $\pi\text{-}\pi^*$ transitions. The relatively weak absorption in the region of 300 to 350 nm might be attributed to the spin-allowed metal-to-ligand charge transfer ($^1\text{MLCT}$) transitions and the weak absorption tail in the range of 450-500 nm might be due to the spin-forbidden $^3\text{MLCT}$ transitions.¹⁴ The photoluminescence spectrum of complex **1** showed the maximum wavelength at 589 nm in 50% acetonitrile in water with the excitation at 365 nm. The broad and featureless characteristic of the photoluminescence spectrum of complex **1** indicates that the emission is originated from the metal-to-ligand excited state, $^3\text{MLCT}$.^{7c}

The selectivity of complex **1** (10 μM) for metal ions was studied by monitoring its phosphorescence changes upon addition of perchlorate salts of various metal ions including Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Ca^{2+} , Ba^{2+} , Fe^{2+} , Cu^{2+} , Ag^+ , Zn^{2+} , Cd^{2+} , Hg^{2+} and Pb^{2+} (20 μM) in 50% acetonitrile in water as shown in Figure 3. The phosphorescence of complex **1** was quenched significantly upon addition of $\text{Cu}(\text{II})$ ion and

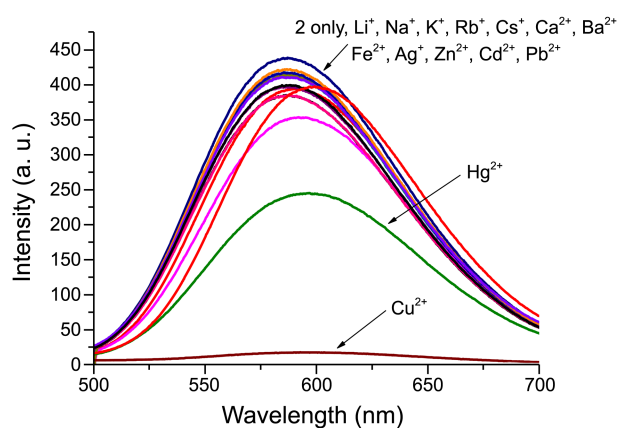


Figure 3. Phosphorescence spectra of iridium(III) complex **1** (10 μM) upon addition of various metal ions (2 equiv) in 50% acetonitrile in water (excitation: 365 nm).

quenched slightly upon addition of $\text{Hg}(\text{II})$ ion, but almost no-quenching was absorbed upon addition of the other metal ions. Figure 4 shows the visual changes of the photoluminescence of complex **1** upon addition of various metal ions, indicating the significant quenching of the photoluminescence upon addition of $\text{Cu}(\text{II})$ ion. The selectivity of complex **1** for various metal ions was graphically demonstrated by the relative emission intensities, I_0/I , where I_0 and I are the maximum emission intensity of iridium(III) complex **1** in

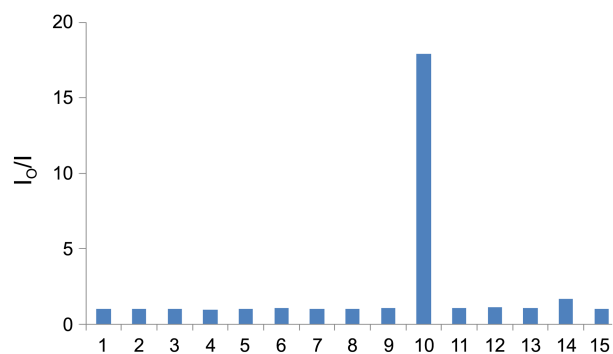


Figure 5. Relative emission intensities of iridium(III) complex **1** (10 μM), given as the ratio I_0/I , upon addition of various metal ions (2 equiv) in 50% acetonitrile in water: complex **1** only (1), Li^+ (2), Na^+ (3), K^+ (4), Rb^+ (5), Cs^+ (6), Ca^{2+} (7), Ba^{2+} (8), Fe^{2+} (9), Cu^{2+} (10), Ag^+ (11), Zn^{2+} (12), Cd^{2+} (13), Hg^{2+} (14) and Pb^{2+} (15).

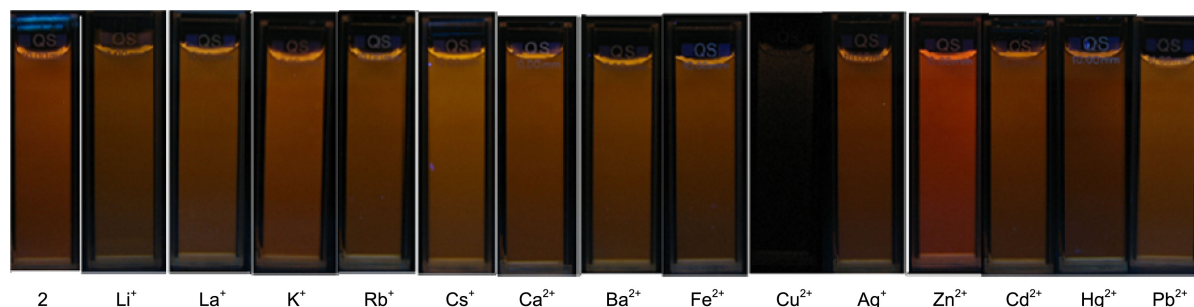


Figure 4. Visualized phosphorescent emission changes of iridium(III) complex **1** (10 μM) upon addition of various metal ions (2 equiv) in 50% acetonitrile in water (obtained with usual laboratory UV lamp, 254 nm).

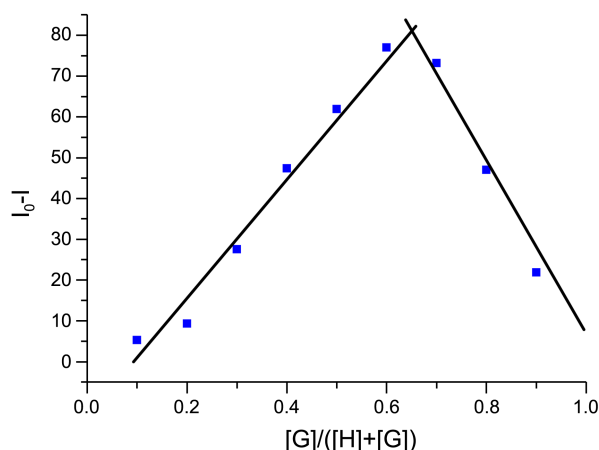


Figure 6. Job's plot for the complex formation between iridium(III) complex **1** and Cu(II) ion in 50% acetonitrile in water.

the absence and presence of metal ion, respectively, as illustrated in Figure 5. The relative emission intensities, I_0/I , were 17.9 for Cu(II) and 1.68 for Hg(II), but they were in the range of 0.95-1.11 for other metal ions. From these results, we can say that the DPA moiety tethered to the 2,2'-bipyridine ligand in complex **1** is quite effective as a selective receptor for Cu(II) ion.

The Job's plot experiment was performed by monitoring the phosphorescence intensity change with the variation of the concentration of both complex **1** and Cu(II) ion. As shown in Figure 6, the maximum was observed at 0.67, indicating the formation of the typical 1:2 complex. Each of the two DPA moieties tethered to the 2,2'-bipyridine ligand in complex **1** seems to be utilized for the complexation with Cu(II) ion.

The phosphorescence titration spectra of complex **1** upon addition of Cu(II) ion in 50% acetonitrile in water are shown in Figure 7. As the concentration of Cu(II) ion was increased, the phosphorescence intensity decreased constantly. Based on the phosphorescence titration spectra, the Stern-

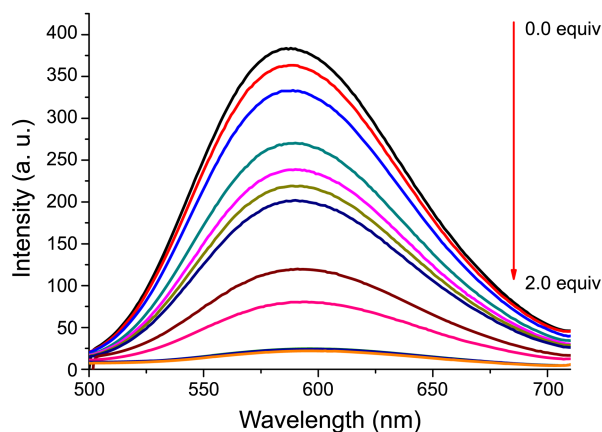


Figure 7. Phosphorescence titration spectra of iridium(III) complex **1** (10 μM) upon addition of Cu(II) ion (0 μM , 2 μM , 4 μM , 7 μM , 8 μM , 9 μM , 10 μM , 12 μM , 14 μM , 16 μM , 20 μM) in 50% acetonitrile in water (excitation: 365 nm).

Volmer constant (K) defining the quenching efficiency for the complexation of iridium(III) complex **1** with Cu(II) ion was calculated to be $5.8 \times 10^4 \text{ M}^{-1}$ according to the Stern-Volmer equation.¹⁵ Similarly, the Stern-Volmer constant (K) for the complexation of iridium(III) complex **1** with Hg(II) ion was calculated to be $2.7 \times 10^4 \text{ M}^{-1}$.

In summary, iridium(III) complex **1** containing two cyclometalating 2-phenylpyridine (ppy) ligands and one 2,2'-bipyridine ligand tethered with two DPA moieties by a methylene linker was prepared. Iridium(III) complex **1** was found to form 1:2 complex selectively with Cu(II) ion with the Stern-Volmer constant of $5.8 \times 10^4 \text{ M}^{-1}$.

Experimental Section

General. The ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer. High-resolution mass spectral data were obtained from the Korea Basic Science Institute Daegu Center (HR-FAB Mass) on a Jeol JMS 700 high resolution mass spectrometer. UV-Vis absorption spectra were obtained with SCINCO S-3100 UV-Vis spectrophotometer. Photoluminescence (PL) spectra were measured on a HITACHI F-7000 fluorescence spectrophotometer. Phosphorescence measurements were carried out by exciting at 365 nm with an excitation band width of 10 nm and an emission band width of 10 nm. The stock solution of iridium(III) complex **1** ($1 \times 10^{-4} \text{ M}$) and perchlorate salts of metal ions ($1 \times 10^{-2} \text{ M}$) were prepared in 50% acetonitrile in water. For phosphorescence measurements, sample solutions were prepared by mixing a measured amount of the stock solution of iridium(III) complex **1** and a measured amount of the stock solution of perchlorate salt of metal ion and then diluting with 50% acetonitrile in water to the desired concentrations of iridium(III) complex **1** and perchlorate salt of metal ion.

Synthesis of Iridium(III) Complex 1. NaH (0.093 g, 3.86 mmol) was dissolved in dry tetrahydrofuran (THF, 10 mL) under an Ar atmosphere. To the NaH solution was added DPA (0.63 mL, 3.51 mmol) dissolved in dry THF (15 mL) through a cannula. The whole mixed solution was stirred for 1 h. The mixed solution was transferred slowly through a cannula into the solution of iridium(III) complex A (Fig. 1, 1.48 g, 1.76 mmol), which was prepared via the reported procedure, in dry THF (15 mL). The whole reaction mixture was stirred at room temperature for 12 h under an Ar atmosphere. After removing the solvent, the residue was dissolved in methylene chloride (20 mL). To the organic solution was added water (20 mL). The mixture was shaken well and, then the organic layer was separated and dried over anhydrous Na_2SO_4 . The solvent was removed and the residue was purified by silica gel chromatography (methylene chloride and methanol, 9:1, v/v) to afford a solid material. The solid material was dissolved into the mixed solvent of methylene chloride and methanol (100 mL, 1:1, v/v). To the solution was added NH_4PF_6 (0.42 g, 2.58 mmol). The whole mixture was stirred at room temperature for 12 h. The solvent was removed and the residue was dissolved in methylene

chloride. To the solution was added water (20 mL). The mixture was shaken well and, then the organic layer was separated and dried over anhydrous Na_2SO_4 . The residue was dissolved in methylene chloride (10 mL). The organic solution was added to diethyl ether (100 mL) drop by drop to induce the formation of a solid material. The solid material was collected using glass filter and dried under high vacuum to afford iridium(III) complex **1** as a yellow solid material. Yield: 0.25 g (66%). mp 145-146 °C; ^1H NMR (300 MHz, CDCl_3) δ 3.93 (s, 8H), 4.03 (s, 4H), 6.24 (d, 2H), 6.87 (t, 2H), 6.99-7.16 (m, 8H), 7.44-7.53 (m, 8H), 7.62-7.78 (m, 12H), 7.87 (d, 2H), 8.48-8.66 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 57.2, 60.2, 119.6, 122.7, 122.9, 123.7, 124.2, 124.7, 124.9, 127.8, 130.9, 131.9, 137.7, 138.1, 143.8, 148.8, 149.1, 151.0, 150.7, 153.2, 155.8, 158.1, 167.9; HRFAB-MS m/z [M^+] calcd. for $\text{C}_{58}\text{H}_{50}\text{IrN}_{10}$ 1079.3849. Found: 1079.3848. IR (KBr pellet) cm^{-1} 3052, 1608, 1478.

Acknowledgments. This research was supported by the National Research Foundation of Korea (grant number: 2011-0005073).

References

- (a) Stern, B. R. *J. Toxicol. Env. Heal. A*, **2010**, *73*, 114. (b) Que, E. L.; Domaille, D. W.; Chang, C. J. *Chem. Rev.* **2008**, *108*, 1517.
- Yardim, M. F.; Budinova, T.; Ekinci, E.; Petrov, N.; Razvigorova, M.; Minkova, V. *Chemosphere* **2003**, *52*, 835.
- (a) Millhauser, G. L. *Acc. Chem. Res.* **2004**, *37*, 79. (b) Seth, R.; Yang, S.; Choi, S.; Sabeen, M.; Roberts, E. A. *Toxicol. in Vitro* **2004**, *18*, 501.
- (a) Royzen, M.; Dai, Z.; Canary, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 1612. (b) Wen, Z.-C.; Yang, R.; He, H.; Jiang, Y.-B. *Chem. Comm.* **2006**, 106. (c) Qi, X.; Jun, E. J.; Xu, L.; Kim, S.-J.; Hong, J. S. J.; Yoon, Y. J.; Yoon, J. *J. Org. Chem.* **2006**, *71*, 2881. (d) Kim, S. H.; Kim, J. S.; Park, S. M.; Chang, S.-K. *Org. Lett.* **2006**, *8*, 371. (e) Xiang, Y.; Tong, A.; Jin, P.; Ju, Y. *Org. Lett.* **2006**, *8*, 2863. (f) Weng, Y.-Q.; Teng, Y.-L.; Yue, F.; Zhong, Y.-R.; Ye, B.-H. *Inorg. Chem. Comm.* **2007**, *10*, 443. (g) Suresh, M.; Ghosh, A.; Das, A. *Chem. Comm.* **2008**, 3906. (h) Kim, H. J.; Hong, J.; Hong, A.; Ham, S.; Lee, J. H.; Kim, J. S. *Org. Lett.* **2008**, *10*, 1963. (i) Khatua, S.; Choi, S. H.; Lee, J.; Huh, J. O.; Do, Y.; Churchill, D. G. *Inorg. Chem.* **2009**, *48*, 1799. (j) Jun, H. S.; Park, M.; Han, D. Y.; Kim, E.; Lee, C.; Ham, S.; Kim, J. S. *Org. Lett.* **2009**, *11*, 3378. (k) Jung, H. S.; Kwon, P. S.; Lee, J. W.; Kim, J. I.; Hong, C. S.; Kim, J. W.; Yan, S.; Lee, J. Y.; Lee, J. H.; Joo, T.; Kim, J. S. *J. Am. Chem. Soc.* **2009**, *131*, 2008. (l) Ballesteros, E.; Moreno, D.; Gomez, T.; Rodríguez, T.; Rojo, J.; García-Valverde, M.; Torroba, T. *Org. Lett.* **2009**, *11*, 1269. (m) Chen, W.; Tu, X.; Guo, X. *Chem. Comm.* **2009**, 1736. (n) Yin, S.; Leen, V.; Snick, S. V.; Boens, N.; Dehaen, W. *Chem. Comm.* **2010**, 6329. (o) Goswami, S.; Sen, D.; Das, N. K. *Org. Lett.* **2010**, *12*, 856. (p) Liu, Z.-C.; Yang, Z.-Y.; Li, T.-R.; Wang, B.-D.; Li, Y.; Qin, D.-D.; Ming-fang Wang, M.-F.; Yan, M.-H. *Dalton Trans.* **2011**, *40*, 9370. (q) Chandrasekhar, V.; Das, S.; Yadav, R.; Hossain, S.; Parihar, R.; Subramaniam, G.; Sen, P. *Inorg. Chem.* **2012**, *51*, 8664.
- Goodall, W.; Williams, J. A. G. *J. Chem. Soc. Dalton Trans.* **2000**, 17, 2893.
- Zhao, Q.; Li, F.; Huang, C. *Chem. Soc. Rev.* **2010**, *39*, 3007.
- (a) Ulbricht, C.; Beyer, B.; Friebe, C.; Winter, A.; Schubert, U. S. *Adv. Mater.* **2009**, *21*, 4418. (b) Song, M.; Park, J. S.; Yoon, M.; Kim, A. J.; Kim, Y.-I.; Gal, Y.-S.; Lee, J. W.; Jin, S.-H. *J. Organomet. Chem.* **2011**, *696*, 2122. (c) Sengottuvelan, N.; Yun, S.-J.; Kang, S. K.; Kim, Y.-I. *Bull. Kor. Chem. Soc.* **2011**, *32*, 4321.
- Ho, M. L.; Hwang, F. M.; Chen, P. N.; Hu, Y. H.; Cheng, Y. M.; Chen, K. S.; Lee, G. H.; Chi, Y.; Chou, P. T. *Org. Biomol. Chem.* **2006**, *4*, 98.
- (a) Zhao, Q.; Cao, T.; Li, F.; Li, X.; Jing, H.; Yi, T.; Huang, C. *Organometallics* **2007**, *26*, 2077. (b) Zhao, Q.; Liu, S.; Li, F.; Yi, T.; Huang, C. *J. Chem. Soc. Dalton Trans.* **2008**, *29*, 3836. (c) Li, Y.; Yoon, U. C.; Hyun, M. H. *Bull. Kor. Chem. Soc.* **2011**, *32*, 122.
- (a) Zhao, Q.; Li, F.; Liu, S.; Yu, M.; Liu, Z. Q.; Yi, T.; Huang, C. *Inorg. Chem.* **2008**, *47*, 9256. (b) You, Y.; Park, S. Y. *Adv. Mater.* **2008**, *20*, 3820. (c) Li, Y.; Hyun, M. H. *Bull. Kor. Chem. Soc.* **2011**, *32*, 4125.
- You, Y.; Han, Y.; Lee, Y.-M.; Park, S. Y.; Nam, W.; Lippard, S. J. *J. Am. Chem. Soc.* **2011**, *133*, 11488.
- Ann, J. H.; Li, Y.; Hyun, M. H. *Bull. Kor. Chem. Soc.* **2012**, *33*, 3465.
- Xu, Z.; Yoon, J.; Spring, D. R. *Chem. Soc. Rev.* **2010**, *39*, 1996.
- Wilde, A. P.; King, K. A.; Watts, R. J. *J. Phys. Chem.* **1991**, *95*, 629.
- (a) Keizer, J. *J. Am. Chem. Soc.* **1983**, *105*, 1494. (b) Cheng, P. P. H.; Silvester, D.; Wang, G.; Kalyuzhny, G.; Douglas, A.; Murray, R. W.; *J. Phys. Chem. B* **2006**, *110*, 4637.