Inorg. Chem. **2004**, *43*, 6896–6898

Inorganic Chemistry

Communication

Synthesis of Ru(II) Complexes of N-Heterocyclic Carbenes and Their Promising Photoluminescence Properties in Water

Seung Uk Son,[†] Kang Hyun Park,[†] Young-Shin Lee,[†] Bo Yun Kim,[†] Cheol Ho Choi,[‡] Myoung Soo Lah,[§] Yun Hee Jang,[†] Du-Jeon Jang,[†] and Young Keun Chung[*,†]

School of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-747, Korea, Department of Chemistry, College of Natural Sciences, Kyungpook National University, Daegu 702-701, Korea, and Department of Chemistry, College of Science, Hanyang University, Ansan, Kyunggi-Do 425-791, Korea

Received April 14, 2004

Novel complexes **1** and **2** based on N-heterocyclic carbenes, which are analogous to Ru(bpy)$_3^{2+}$ and Ru(terpy)$_2^{2+}$, respectively, were synthesized. The complex, which is analogous to Ru(terpy)$_2^{2+}$, exhibited promising photoluminescence properties with a long lifetime of 820 ns in acetonitrile and 3100 ns in water at room temperature, respectively. In addition, ab initio calculations were carried out.

Complex Ru(bpy)$_3^{2+}$ and its derivatives have received considerable attention as potential chromophoric components in such diverse research fields such as light emitting devices, artificial photosynthesis, light emitting sensors, etc.[1] However, complexes of the Ru(bpy)$_3^{2+}$ family are unsuitable for the construction of supramolecular systems, from geometric and synthetic viewpoints.[2] From the purely structural and synthetic viewpoints, terpyridine-based ligands are particularly useful for the design of linear multimetallic component systems. However, in contrast to Ru(bpy)$_3^{2+}$, the complex Ru(terpy)$_2^{2+}$ has not attracted a great deal of attention as a result of its poor photochemical properties (in particular, very weak luminescence and short excited state lifetimes at room temperature, rt). In order to improve the lifetime of the excited state of Ru(terpy)$_2^{2+}$ at rt, many theoretical explanations have been proposed, and various experiments have been attempted.[3] For example, the entrapment of Ru(terpy)$_2^{2+}$ in Y-zeolite dramatically increased the ^{3}MLCT state lifetime (140 ns in an aqueous suspension at rt).[3c] Some Ru(terpy)$_2^{2+}$ derivatives exhibited lifetimes of 200 ns at room temperature.[3j]

Recently, N-heterocyclic carbene (NHC) ligands have become universal ligands in organometallic and inorganic chemistry.[4] Because of their specific coordination chemistry, NHCs stabilize and activate metal centers and, in some cases, can replace organophosphanes. Moreover, NHCs have a much higher trans effect than N- or P-donors and are more tightly bound to the metal.[5] However, their photophysical and -chemical properties have been relatively less well

---

[*] To whom correspondence should be addressed. E-mail: ykchung@plaza.snu.ac.kr.

[†] Seoul National University.

[‡] Kyungpook National University.

[§] Hanyang University.

(1) (a) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. (b) Sauvage, J.-P.; Collins, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigellentti, F.; Cola, L. De; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993. (c) Balzani, V.; Juris, A.; Venturi, M. *Chem. Rev.* **1996**, *96*, 759. (d) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515. (e) Erkkila, K. E.; Dodom, D. T.; Barton, J. K. *Chem. Rev.* **1999**, *99*, 2777. (f) Sun, L.; Hammarström, L.; Akermark, B.; Styring, S. *Chem. Soc. Rev.* **2001**, *30*, 36. (g) Dürr, H.; Bossmann, S. *Acc. Chem. Res.* **2001**, *34*, 905. (h) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892. (i) Yersin, H.; Kratzer, C. *Coord. Chem. Rev.* **2002**, *229*, 75. (j) De Cola, L.; Belser, P. *Coord. Chem. Rev.* **1998**, *177*, 301. (k) Blanco, M.-J.; Jiménez, M. C.; Chambron, J.-C.; Heitz, V.; Linke, M.; Sauvage, J.-P. *Chem. Soc. Rev.* **1999**, *28*, 293.

(2) (a) Collin, J.-P.; Guillerez, S.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1989**, 116. (b) Constable, E. C.; Cargill Thompson, A. M. W. *J. Chem. Soc., Dalton Trans.* **1992**, 2947. (c) Constable, E. C.; Edwards, A. J.; Martinez-Maez, R.; Raithby, P. R.; Cargill Thompson, A. M. W. *J. Chem. Soc., Dalton Trans.* **1994**, 645. (d) MacDonnell, F. M.; Ali, M. D. M.; Kim, M. J. *Comments Inorg. Chem.* **2000**, *22*, 203. (e) von Zelewsky, A., Mamula, O. *J. Chem. Soc., Dalton Trans.* **2000**, 219.

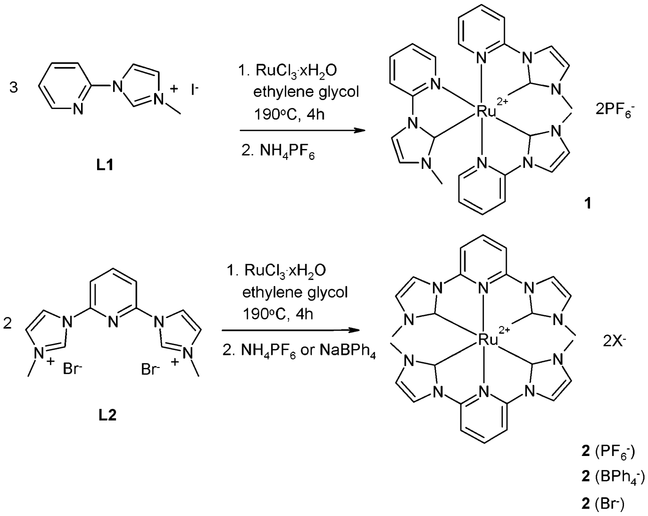
(3) (a) Hecker, C. R.; Gushurst, A. K. I.; McMillin, D. R. *Inorg. Chem.* **1991**, *30*, 538. (b) Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Cargill Thompson, A. M. W. *Inorg. Chem.* **1995**, *34*, 2759. (c) Bhuiyan, A. A.; Kincaid, J. R. *Inorg. Chem.* **1998**, *37*, 2525. (d) Ceroni, P.; Credi, A.; Balzani, V.; Campagna, S.; Hanan, G. S.; Arana, C. R.; Lehn, J.-M. *Eur. J. Inorg. Chem.* **1999**, *1409*. (e) Constable, E. C.; Housecroft, C. E.; Schofield, E. R.; Encinas, S.; Armaroli, N.; Barigelletti, F.; Flamingli, L.; Figgemeier, E.; Vos, J. G. *Chem. Commun.* **1999**, 869. (f) El-ghayoury, A.; Harriman, A.; Khatyr, A.; Ziessel, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 185. (g) El-ghayoury, A.; Harriman, A.; Khatyr, D.; Ziessel, R. *J. Phys. Chem. A* **2000**, *104*, 1512. (h) Liegghio, R.; Potvin, P. G.; Lever, A. B. P. *Inorg. Chem.* **2001**, *40*, 5485. (i) Polson, M. I. J.; Taylor, N. J.; Hanan, G. S. *Chem. Commun.* **2002**, 1356. (j) Fang, Y.-Q.; Tayler, N. J.; Hanan, G. S.; Loiseau, F.; Passalacoqua, R.; Campagna, S.; Nierengarten, H.; Van Dorsselaer, A. *J. Am. Chem. Soc.* **2002**, *124*, 7912. (k) Passalacqua, R.; Loiseau, F.; Campagna, S.; Fang, Y.-Q.; Hanan, G. S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1608. (l) Harriman, A.; Khatyr, A.; Ziessel, R. *J. Chem. Soc., Dalton Trans.* **2003**, 2061.

(4) (a) Hermann, W. A.; Kocher, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 2162. (b) Hermann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.

(5) (a) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023. (b) Grundemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2001**, *20*, 5485.

10.1021/ic049514f CCC: $27.50

Scheme 1. Synthetic Method for New Compounds



studied.[6] In the course of this study on the use of NHC complexes,[7] complexes **1** and **2**(PF_6^-), which are analogous to Ru(bpy)$_3^{2+}$ and Ru(terpy)$_2^{2+}$, respectively, were synthesized, and their photochemical properties were studied. This paper presents our results of the synthesis and photochemical properties of complexes **1** and **2**(PF_6^-) along with their relevance to Ru(bpy)$_3^{2+}$ and Ru(terpy)$_2^{2+}$.

Complex **1** was prepared in a 75% yield by the complexation of $RuCl_3$ with ligand **L1** in a refluxing ethylene glycol solution (Scheme 1). Peris et al. reported[8] a ruthenium NHC complex with the same skeleton as complex **2**(PF_6^-) and used it as a catalyst in the hydrogen transfer reaction and oxidative cleavage of olefins.

In the synthesis of Ru(NHC)$_3^{2+}$ derivatives, there is always a problem as a result of the selectivity between the *mer*- and *fac*-isomer. The latter is known to be the thermodynamically more stable form and is obtained as a major product in almost all cases.[9] Interestingly, in contrast to our prediction, the *mer*-isomer was obtained as the sole product, which was confirmed by a ^{1}H NMR study of complex **1** showing two methyl peaks at a 1:2 ratio.[10] Next, ligand **L2** was synthesized using the method reported in the literature[11] and successfully used in the synthesis of complexes **2**(PF_6^-), **2**(BPh_4^-), and **2**(Br^-) by the complexation with $RuCl_3$ in refluxing ethylene glycol. The molecular structure of complex **2**(BPh_4^-) was confirmed by X-ray diffraction (Figure 1).[12] The two ligands are mutually arranged about each metal center in an almost orthogonal manner. The resulting local environment around the Ru^{2+} cation is therefore pseudo-orthogonal (D_{2d}) with a conformational restriction imposed by the presence of methyl groups on ligand **L2**.

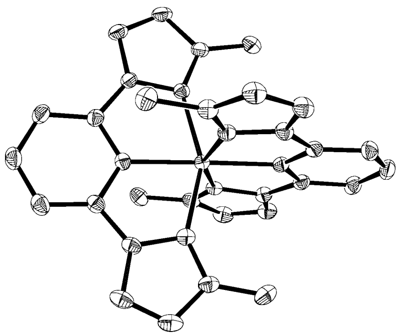


Figure 1. ORTEP drawing of **2**(BPh_4^-) with 30% ellipsoid probability (counteranions (BPh_4^-) were omitted for clarity).

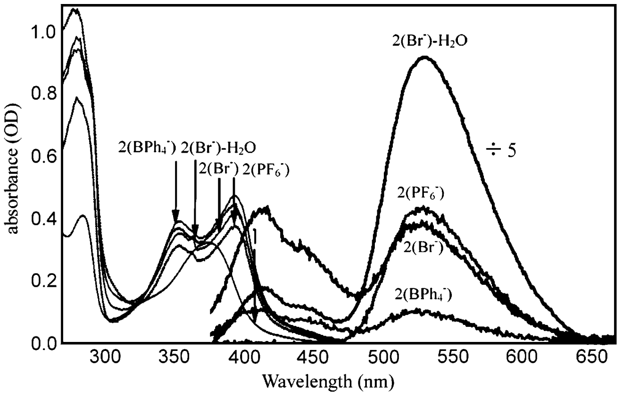


Figure 2. Absorption and emission spectra, with excitation at 354 nm, of Ru^{2+} complexes in acetonitrile (if not specified) and water under argon.

The photophysical properties of complexes **1** and **2**(PF_6^-) were investigated in order to make a comparison with those of Ru(bpy)$_3^{2+}$ and Ru(terpy)$_2^{2+}$. Complex **1**, compared with Ru(bpy)$_3^{2+}$, shows a blue-shifted λ_{max} (368 nm) in the absorption spectrum presumably due to the electron-rich property of the NHC ligands (Figure 2 and Table 1).

The voltammetric oxidation of complexes **1** and **2**(PF_6^-) occurred as a chemically reversible 1-electron process at a scan rate of 100 mV/s (see Supporting Information, SI). As expected, $E_{1/2}$ for $\mathbf{2}^{2+}/\mathbf{2}^{3+}$ was similar to that of $\mathbf{1}^{2+}/\mathbf{1}^{3+}$, but lower than those of Ru(bpy)$_3^{2+}$ and Ru(terpy)$_2^{2+}$ due to the electron-donating nature of NHC, which is consistent with

---

(6) (a) Xue, W.-M.; Chan, M. C.-W.; Su, Z.-M.; Cheung, K.-K.; Liu, S.-T.; Che, C.-M. *Organometallics* **1998**, *17*, 1622. (b) Liu, Q.-X.; Xu, F.-B.; Li, Q.-S.; Zeng, X.-S.; Leng, X.-B.; Chou, Y. L.; Zhang, Z.-Z. *Organometallics* **2003**, *22*, 309. (c) Liu, Q.-X.; Song, H.-B.; Xu, F.-B.; Li, Q.-S.; Zeng, X.-S.; Leng, X.-B.; Zhang, Z.-Z. *Polyhedron* **2003**, *22*, 1515.

(7) (a) Seo, H.; Park, H.-J.; Lee, K. H.; Kim, B. Y.; Son, S. U.; Chung, Y. K. *Organometallics* **2003**, *22*, 618. (b) Seo, H.; Park, H.-J.; Kim, B. Y.; Lee, J. H.; Son, S. U.; Chung, Y. K. *Organometallics* **2003**, *22*, 4783. (c) Park, K. H.; Son, S. U.; Kim, S. Y.; Seo, H. M.; Chung, Y. K. *Eur. J. Org. Chem.* **2003**, 4341.

(8) Poyatos, M.; Mata, J. A.; Falomir, E.; Crabtree, R. H.; Peris, E. *Organometallics* **2003**, *22*, 1110.

(9) (a) King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc*. **1985**, *107*, 1431. (b) Colombo, M. G.; Brunold, T. C.; Riedener, T.; Güdel, H. U.; Fortsch, M.; Bürgi, H.-B. *Inorg. Chem.* **1994**, *33*, 545. (c) Dedeian, K.; Djurovich, P. I.; Garces, F. O.; Carlson, G.; Watts, R. J. *Inorg. Chem.* **1991**, *30*, 1685. (d) Grushin, V. V.; Herron, N.; LeCloux, D. D.; Marshall, W. J.; Petrov, V. A.; Wang, Y. *Chem. Commun.* **2001**, 1494.

(10) This result may be due to the steric requirement of the ligand. Recently, Fletcher et al. reported the isolation and purification of tris(2,2′-bipyridine) complexes of ruthenium(II) containing unsymmetrical ligands. They found that the relative yield of the facial isomer was decreased with increasing the steric bulk, preventing the isolation of *fac*-[Ru(L)]$_3$]$^{2+}$. Fletcher, N. C.; Nieuwenhuyzen, M.; Rainey, S. *J. Chem. Soc., Dalton Trans.* **2001**, 2641.

(11) (a) Chen, J. C. C.; Lin, I. J. B. *J. Chem. Soc., Dalton Trans.* **2000**, 839. (b) Grunedemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 10473.

(12) Many attempts to solve the single crystal structure of **2**(PF_6^-) by an X-ray diffraction study were unsuccessful due to the disorder caused by PF_6^- anions. Thus, we screened various counteranions such as nethavanadate, nitrate, tetrafluoroborate, molybdate, persulfate, and tetraphenylborate. When tetraphenylborate was used as a counteranion, single crystals of **2**(BPh_4^-) suitable for an X-ray study were obtained.

Table 1. Spectroscopic Properties of Ru^{2+} Complexes[a]

complex	λ_{max}^{abs} (nm)	ϵ (10^3 M^{-1} cm^{-1})	λ_{max}^{em} (nm)	rel em int[b]	decay time (ns)
$Ru(bpy)_3^{2+}$	450	14.3	597	3.83	860[c]
$Ru(terpy)_2^{2+}$	474	17.2			0.25[d]
1	368	11.7			
2(PF_6^-)	343, 382	11.6, 15.2	532	1.04	820
2(BPh_4^-)	343, 382	15.6, 20.1	532	0.39	490
2(Br^-)	343, 382	13.0, 16.8	532	1.00	600
2(Br^-)-H_2O	341, 381	13.8, 17.3	532	9.90	3100

[a] 2.33×10^{-5} M in acetonitrile (if not specified) and water at room temperature. [b] Relative maximum intensity at emission. [c] Reference 1. [d] Reference 15.

a high energy for HOMO. The increase in the energy of the HOMO suggests a red shift in the absorption spectrum. However, as already mentioned, the experimental observation shows a blue shift in the absorption spectrum. It is possible that NHC has a higher electron density than terpy, and a higher lying π^* orbital. Therefore, it is expected that the increase in the LUMO energy in complex **2**(PF_6) is higher than that of $Ru(terpy)_2^{2+}$, which is consistent with the DFT calculation (see calculated HOMO and LUMO orbital energies in SI). This would mean that the blue shift is essentially a LUMO effect.

Complex **1** is nonemissive in acetonitrile at room temperature. However, complex **2**(PF_6^-) has very promising photophysical properties. It shows a different absorption spectrum from that of $Ru(terpy)_2^{2+}$ (Figure 2 and Table 1). The complex **2**(PF_6^-) shows two absorption peaks, 343 and 382 nm. Compared with those of $Ru(bpy)_3^{2+}$ and $Ru(terpy)_2^{2+}$, the two peaks were highly blue-shifted. Using ab initio calculations, it was provisionally determined that the two blue-shifted peaks arose from the MLCT. In contrast to $Ru(terpy)_2^{2+}$, complex **2**(PF_6^-) shows a very strong emission with a maximum at 532 nm.[13] The 3D emission spectrum was examined by changing the excitation wavelength (see SI). The pattern of the resultant 3D emission peak was almost the same as that of the absorption spectrum, indicating that the emission peak at 532 nm originated from complex **2**(PF_6^-), and not from impurities.[14]

The emission kinetics at 532 nm in Figure 3 shows a long lifetime of 820 ns in acetonitrile at room temperature, which is 3280 times larger than that (0.25 ns) of $Ru(terpy)_2^{2+}$.[15b] In artificial photosynthesis, the lifetime of the chromophore in water is very important.[16] In order to measure its lifetime in H_2O, complex **2**(Br^-) with Br^- as the counteranion was synthesized. The lifetimes of complex **2**(Br^-) were 600 ns in acetonitrile and 3100 ns in H_2O, i.e., 12400 times larger than that of $Ru(terpy)_2^{2+}$[1a] (Table 1 and Figure 3). To the best of our knowledge, the lifetime of complex **2**(Br^-) in water is the longest among the reported luminescence lifetimes of the $Ru(terpy)_2^{2+}$ derivatives. This observation is quite unprecedented because MLCT chromophores generally show shorter lifetimes in water than in organic solvents.[17] As shown in Table 1, the counteranions strongly influence the luminescence lifetimes of the chromophore.[18]

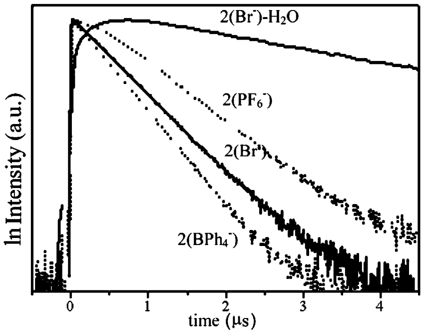


Figure 3. Emission kinetic curves excited at 355 nm and monitored at 532 nm, of Ru^+ complexes in acetonitrile (if not specified) and water under argon.

In conclusion, complexes **1** and **2**(PF_6^-) were synthesized on the basis of NHC. Complex **2**(PF_6^-) showed very promising photoluminescence properties in water, and it is expected that this complex can be a complement or substitute for $Ru(bpy)_3^{2+}$ in many fields. Compound **2**(PF_6^-) represents an alternative molecular design that imparts a green photoluminescence into a synthetically facile system. Counteranions play important roles in the luminescence quenching of the rigid chromophore. Future research will be focused on obtaining a theoretical explanation of the photophysical properties, the synthesis of the derivatives of complexes **1** and **2**(PF_6^-) with a variety of functional groups, and the application of these compounds.

Acknowledgment. This work was supported by the Korea Science Engineering Foundation (KOSEF 1999-1-12200-001-1) and the Brain Korea 21 Program. D.-J.J. thanks the Strategic National R&D Program (M1-0214-00-0108).

Supporting Information Available: Detailed experimental procedures and characterization data, cyclic voltammetry study, 3D emission study, ab initio calculation. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049514F

---

(13) We are pursuing to discover the origin of the differencies in photophysical properties between **1** and **2**(PF_6^-) using ab initio calculation.

(14) The fluorescence spectra in the range 400−500 nm can be assigned as ^{1}MLCT because of two reasons. The first one is that the fluorescence spectrum in the range 400−500 nm is the approximate mirror image of absorption spectrum (please see Figure 2). The second reason is that the fluorescence excitation spectrum monitored at 440 nm corresponds to the absorption spectrum (see SI for excitation spectrum).

(15) (a) Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 5129. (b) Winkler, J. R.; Netzel, T. L.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1987**, *109*, 2381.

(16) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163.

(17) (a) Richter, M. M.; Bard, A. J. *Anal. Chem.* **1998**, *70*, 310. (b) Bruce, D.; Richter, M. M. *Anal. Chem.* **2002**, *74*, 1340.

(18) This means that the interactions between counteranions and the chromophore have a strong influence on the decay time. This phenomenon can arise due to the frozen motion of the ligand and the effect of the counteranions in emission quenching by acting as energy dissipaters and/or sinks. In water, the effect of the counteranion may be less presumably due to the slow diffusion-influenced quenching rate in water compared to that in acetonitrile. We believe that there may be charge redistribution in going from the singlet state to the triplet state. The water solvent has a longer longitudinal relaxation time, so that it is expected to retard the intersystem crossing rate.