

## Electrochemiluminescence: ECL Luminophores and Applications

Jin Ho Bang

Materials Literature Seminar

December 2, 2004

Electrochemiluminescence (ECL) is the phenomenon that involves electron transfer reaction between two charged species generated on electrode surface to form an excited-state that emits light.<sup>1</sup> The excited state generated in ECL is the same as that in photoluminescence (PL). However, the absence of light source to get an excited state allows ECL to be a more powerful analytical tool since it will give a lower detection limit and higher selectivity.

ECL can be generated by many different ways but the most general mechanism for ECL generation is annihilation mechanism.<sup>2a</sup> In this mechanism, ECL occurs by electron transfer reaction between oxidized and reduced species, both of which are generated at the electrode. Also, two different precursors can be used to generate ECL generation. This involves cross-reaction between a radical cation of one species and a radical anion of a different species to produce an excited state. This mechanism is referred to as annihilation cross-reaction.<sup>2b</sup> On the other hand, unidirectional single potential step or sweep can be used to generate ECL along with the use of a co-reactant.<sup>2c</sup> A co-reactant produces a strong oxidant or reductant that will react with an ECL luminophore to generate an excited state via bond cleavage upon electrochemical oxidation or reduction. Co-reactant allows efficient ECL generation even in aqueous solution by avoiding water oxidation or reduction and makes ECL a useful analytical technique for many interesting applications such as enzymatic biosensors and immunoassays.

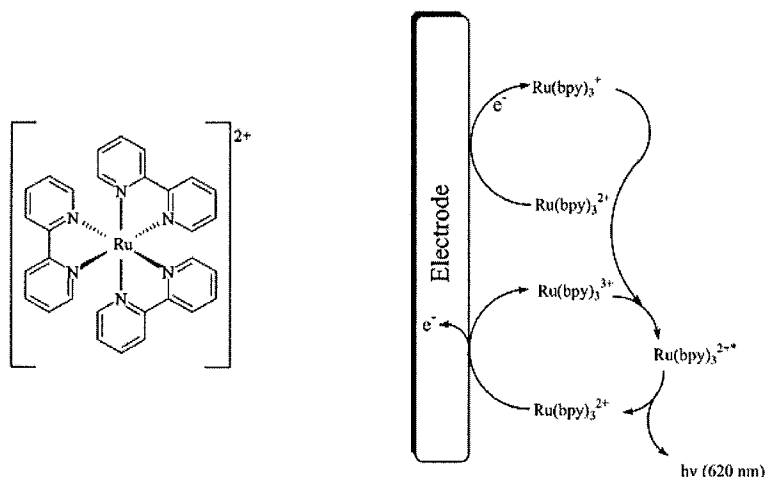


Figure 1. Structure of Ru(bpy)<sub>3</sub><sup>2+</sup> and proposed mechanism for ECL generation.

ECL luminophores can be categorized into two large groups: one is transition metal-based inorganic complexes and the other is organic compounds. The first ECL phenomenon was observed in an organic compound, however, inorganic complexes are the focus of research because of their high ECL efficiency. Since the first inorganic ECL luminophore was reported in 1972 (Figure 1), there have been many studies on a variety of different transition metal complexes leading to increased ECL efficiency. Ru(bpy)<sub>3</sub><sup>2+</sup>, the first inorganic complex to show ECL has played an important role in both fundamental studies and commercial applications showing high efficiency and stability. The Ru(bpy)<sub>3</sub><sup>2+</sup> moiety has been utilized in many interesting

systems to label biomolecules and modified to detect metal ions coupled with crown ethers.<sup>3,4</sup> In addition, there has been some efforts to increase the intensity of ECL using dendrimetic molecule containing multiple Ru(bpy)<sub>3</sub><sup>2+</sup> units.<sup>5</sup>

Besides ruthenium complexes, osmium- and iridium-based complexes have attracted interest for ECL luminophores. Even though it was reported that ECL efficiencies of Os(bpy)<sub>3</sub><sup>2+</sup> and Os(phen)<sub>3</sub><sup>2+</sup> were weaker than that of Ru(bpy)<sub>3</sub><sup>2+</sup>, a great increase in ECL intensity was observed by ligand tuning. Os(phen)<sub>2</sub>(dppene)<sup>2+</sup> showed higher photoluminescence quantum efficiency and the redox behavior was more stable.<sup>6</sup> More recently, iridium complexes were found to be easy to tune the frequency of luminescence (from blue to red) by simply changing the bound ligands.<sup>7</sup> Bis(3,5-difluoro-2-(2-pyridyl)phenyl)-(2-carboxypyridyl)iridium(III) showed ECL maximum peak that is substantially blue-shifted from that of Ru(bpy)<sub>3</sub><sup>2+</sup>, suggesting possible applications for multi-analyte detection.<sup>8</sup>

ECL was also observed in semiconductor nanocrystals such as Si.<sup>9</sup> One of the interesting features of ECL from Si nanocrystals is the red-shifted ECL maximum peak compared to PL maximum peak. This shift is closely related to surface states of Si nanocrystals.

ECL has found applications in many areas. It has showed its usefulness in the detection systems of high performance liquid chromatography (HPLC) and capillary electrophoresis (CE). By attaching ECL luminophores to biomolecules, it can be used for enzymatic biosensor, immunoassay, and DNA-probe assay.<sup>10-11</sup> Also, there has been an interesting result regarding lasing action driven by ECL.<sup>12</sup> Recently tremendous efforts have been made to solid-state light emitting devices as a potential application of ECL since 1996.<sup>13</sup>

## References

1. (a) M. M. Richter, "Electrochemiluminescence (ECL)," *Chem. Rev.* **2004**, *104*, 3003-3036. (b) K. A. Fahrnich, M. Pravda, G. G. Guilbault, "Recent applications of electrogenerated chemiluminescence in chemical analysis," *Talanta* **2001**, *54*, 531-559.
2. (a) N. Tokel, A. J. Bard, "Electrogenerated chemiluminescence. IX. Electrochemistry and emission from systems containing tris(2,2'-bipyridine)ruthenium(II) dichloride," *J. Am. Chem. Soc.* **1972**, *94*, 2862-2863. (b) E. M. Gross, J. D. Anderson, A. F. Slaterbeck, S. Thayumanavan, S. Barlow, Y. Zhang, S. R. Marder, H. K. Hall, M. Flore Nabor, J.-F. Wang, E. A. Mash, N. R. Armstrong, R. M. Wightman, "Electrogenerated chemiluminescence from derivatives of aluminum quinolate and quinacridones: Cross-reactions with triaryl amines lead to singlet emission through triplet-triplet annihilation pathways," *J. Am. Chem. Soc.* **2000**, *122*, 4972-4979. (c) H. S. White, A. J. Bard, "Electrogenerated chemiluminescence. 37. Aqueous ECL systems based on tris(2,2'-bipyridine)ruthenium(2+) and oxalate or organic acids," *J. Am. Chem. Soc.* **1981**, *103*, 512-516.
3. (a) G. F. Blackburn, H. P. Shah, J. H. Kenten, J. Leland, R. A. Kamin, J. Link, J. Peterman, M. J. Powell, A. Shah, D. B. Talley, "Electrochemiluminescence detection for development of immunoassays and DNA probe assays for clinical diagnostics," *Clin. Chem.* **1991**, *37*, 1534-1539. (b) J. H. Kenten, S. Gudiband, J. Link, J. J. Willey, B. Curfman, E. O. Major, R. J. Massey, "Improved electrochemiluminescent label for DNA probe assays: rapid quantitative assays of HIV-1

- polymerase chain reaction products,” *Clin. Chem.* **1992**, *38*, 873-879.
4. R. Y. Lay, M. Chiba, N. Kitamura, A. J. Bard, “Electrogenerated chemiluminescence. 68. Detection of sodium ion with a ruthenium(II) complex with crown ether moiety at the 3,3'-positions on the 2,2'-bipyridine ligand,” *Anal. Chem.* **2002**, *74*, 551-553.
  5. (a) M. Zhou, J. Roover, “Dendrimeric supramolecular assembly with multiple Ru(II) tris(bipyridine) units at the periphery: Synthesis, spectroscopic, and electrochemical study,” *Macromolecules* **2001**, *34*, 244-252. (b) M. Zhou, J. Roover, G. P. Robertson, C. P. Grover, “Multilabeling biomolecules at a single site. 1. Synthesis and characterization of a dendritic label for electrochemiluminescence assays,” *Anal. Chem.* **2003**, *75*, 6708-6717.
  6. D. Bruce, M. M. Richter, K. J. Brewer, “Electrochemiluminescence from  $\text{Os}(\text{phen})_2(\text{dppene})^{2+}$  (phen = 1,10-phenanthroline and dppene = bis(diphenylphosphino)ethene),” *Anal. Chem.* **2002**, *74*, 3157-3159.
  7. Md. K. Nazeeruddin, R. Humphry-Baker, D. Berner, S. Rivier, L. Zuppiroli, M. Graetzel, “Highly Phosphorescence Iridium Complexes and Their Application in Organic Light-Emitting Devices,” *J. Am. Chem. Soc.* **2003**, *125*, 8790-8797.
  8. B. D. Muegge, M. M. Richter, “Multicolored electrogenerated chemiluminescence from ortho-metalated iridium(III) systems,” *Anal. Chem.* **2004**, *76*, 73-77.
  9. Z. Ding, B. M. Quinn, S. K. Haram, L. E. Pell, B. A. Korgel, A. J. Bard, “Electrochemistry and electrogenerated chemiluminescence from silicon nanocrystal quantum dots,” *Science* **2002**, *296*, 1293-1297.
  10. F. Jameison, R. I. Sanchez, L. Dong, J. K. Leland, D. Yost, M. T. Martin, “Electrochemiluminescence-based quantitation of classical clinical chemistry analytes,” *Anal. Chem.* **1996**, *68*, 1298-1302.
  11. W. Miao, A. J. Bard, “Electrogenerated chemiluminescence. 72. Determination of immobilized DNA and C-reactive protein on Au(111) electrodes using tris(2,2'-bipyridyl)ruthenium(II) labels,” *Anal. Chem.* **2003**, *75*, 5825-5834.
  12. T. Horiuchi, O. Nawa, N. Hatakenaka, “Evidence for laser action driven by electrochemi-luminescence,” *Nature* **1998**, *394*, 659-661.
  13. (a) J. Slinker, D. Bernards, P. L. Houston, H. D. Abruna, S. Bernhard, G. G. Malliaras, “Solid-state electroluminescent devices based on transition metal complexes,” *Chem. Comm.* **2003**, *19*, 2392-2399. (b) J. -K. Lee, D. S. Yoo, E. S. Handy, M. F. Rubner, “Thin film light emitting devices from an electroluminescent ruthenium complex,” *Appl. Phys. Lett.* **1996**, *69*, 1686-1688. (c) C. H. Lyons, E. D. Abbas, J. -K. Lee, M. F. Rubner, “Solid-state light-emitting devices based on the trischelated ruthenium(II) complex. 1. Thin film blends with poly(ethylene oxide),” *J. Am. Chem. Soc.* **1998**, *120*, 12100-12107. (d) H. Rudmann, M. F. Rubner, “Single layer light-emitting devices with high efficiency and long lifetime based on tris(2,2' bipyridyl) ruthenium(II) hexafluorophosphate,” *J. Appl. Phys.* **2001**, *90*, 4338-4345. (e) H. Rudmann, S. Shimada, M. F. Rubner, “Solid-state light-emitting devices based on the trischelated ruthenium(II) complex. 4. High-efficiency light-emitting devices based on derivatives of the tris(2,2' bipyridyl) ruthenium(II) complex,” *J. Am. Chem. Soc.* **2002**, *124*, 4918-4921.