Manipulation of Absorption Maxima by Controlling Oxidation Potentials in Bis(tridentate) Ru(II) N-Heterocyclic Carbene Complexes

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A series of seven Ru(II) complexes bearing NHC ligands have been synthesized. The electronic structures of these complexes were analysed by spectroscopic and electrochemical methods and further examined by theoretical calculations. Data show that absorption maxima are dependent on the HOMO level rather than the HOMO-LUMO gaps.

Key Words : Ru, NHC, Polypyridyl, MLCT, Redox potential, Ligand field

Introduction

Manipulation of absorption maxima ($\lambda_{\text{max}}$) as well as oscillator strengths of light harvesting chromophores is crucial in solar energy conversion-related applications. In many organic and inorganic systems, $\lambda_{\text{max}}$ values are strongly correlated with HOMO and LUMO levels. Destabilization and stabilization of HOMO and LUMO, respectively, are common approaches to increase $\lambda_{\text{max}}$ values. Such approaches can be applied to Ru(II) polypyridyl complexes, in which the nature of the electronic transitions in low energy region is characteristic of Ru-based occupied molecular orbitals (MOs)-to-ligand-based virtual MOs charge transfer. A strategy for stabilizing virtual MOs includes expanding conjugation of the ligand or incorporating electron withdrawing groups to the periphery of the ligand. One of the representative methods of destabilizing occupied MOs involves applying a strong ligand field. Toward these ends, a huge numbers of new ligand systems that include N, C, or S donor moiety have been developed in addition to the conventional polypyridyl ligands such as 2,2'-bipyridine (bpy) and 2,2',6,2''-terpyridine (tpy) derivatives.

We have previously exploited N-heterocyclic carbene (NHC) compounds, 2-(3-methylimidazolium-1-yl)pyridine (mip) or 2,6-bis-(3-methylimidazolium-1-yl)pyridine (bip), as bidentate or tridentate ligands, respectively, for a new type of ruthenium chromophore. Electrochemical data as well as theoretical calculation data of [Ru(bip)$_2$]$^{2+}$, for example, indicate that HOMO of this complex is ca. 0.2 V more destabilized relative to that of [Ru(tpy)$_2$]$^{2+}$ benchmark, as intended to bring a strong ligand field. However, the degree of destabilization of LUMO is even larger due to a confined electronic delocalization within the pyridyl ring. When one bip ligand is replaced with 2,2',6,2''-terpyridine-4'-carboxylic acid (CTN, Scheme 1), the tpy-localized virtual orbital becomes the LUMO of the molecule, while a Ru-based occupied orbital whose energy is destabilized by the bip ligand still remains a HOMO. The $\lambda_{\text{max}}$ value was brought back to visible region (463 nm). Dinda et al. reported that using 1,1'-[2,6-pyridinediylbis(methylene)]bis[3-methylimidazolyl] ligand to augment the ligand field gave rise to 0.44 and 0.24 V destabilization of HOMO levels for homoleptic [RuL$_2$]$^{2+}$ and heteroleptic [Ru(tpy)L]$^{2+}$ (L=1,1'-[2,6-pyridinediylbis(methylene)]-bis[3-methylimidazolyl]), respectively, relative to that of [Ru(tpy)$_2$]$^{2+}$. The $\lambda_{\text{max}}$ values were 429 and 500 nm and molar extinction coefficient ($\epsilon$) were 12000 and 5200 M$^{-1}$cm$^{-1}$, respectively. These results highlight the capacity of NHC compound as a versatile ligand for strong ligand field effects.

Although the heteroleptic approach mentioned above works for manipulating the $\lambda_{\text{max}}$ values of Ru complexes to some extent, there is a need to find the factors that govern the $\lambda_{\text{max}}$ values of Ru(NHC) complexes to exploit such systems further. Under this background, combined with the lack of information regarding systematic structure-property relationships of Ru(NHC) systems, we have newly synthesized seven Ru complexes that possess a heteroleptic [Ru(tpy)-(NHC)]$^{2+}$ or a homoleptic [Ru(NHC)$_2$]$^{2+}$ topology and feature NNC- or NN^C-type NHC structural motif (NN = bipyridyl, C = azolyl, and ^ = methylene). The structures of series complexes are shown in Scheme 2.

The synthesis of NNC- or NN^C-type ligands and their transition metal complexes have been reported in a handful of literature. However, the background for employing such ligand systems to build a new series of Ru complexes

A series of seven Ru(II) complexes bearing NHC ligands have been synthesized. The electronic structures of these complexes were analysed by spectroscopic and electrochemical methods and further examined by theoretical calculations. Data show that absorption maxima are dependent on the HOMO level rather than the HOMO-LUMO gaps.

methyl-2,2′-bipyridine,9(b) (2,2′,6′,2′′-tepyridine)(trichloro)-Ru(III) (Ru(tpy)Cl3)9(c) were prepared according to literature procedures. Column chromatography was performed on silica gel 60 (230-400 Mesh, Merck).

**Instrumentation.** 1H and 13C NMR spectra were recorded with Bruker (75 MHz for 1H NMR), Agilent (400 MHz and 100 MHz for 1H and 13C NMR, respectively) and Agilent (500 MHz and 125 MHz for 1H and 13C NMR, respectively) spectrometers. 1H NMR spectra were taken in CDCl3 and DMSO-d6 and were referenced to residual CDCl3 (7.27 ppm) and DMSO-d6 (2.50 ppm), respectively. Chemical shifts of the 13C NMR spectra were measured relative to CDCl3 (77.16 ppm) or DMSO-d6 (39.52). Elemental analyses were done at the National Center for Inter-University Research Facilities located in the Seoul National University. High-resolution mass spectrometry (HRMS) data were obtained at the Koreas Basic Science Institute (Daegu). Electronic absorption spectra were recorded on a Beckman Du-650 spectrophotometer. Cyclic voltammograms were obtained with a CH Instrument voltammetric analyzer. Measurements were performed after the acetonitrile (spectroscopic grade) solution was purged with dry nitrogen gas for 30 min. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6). Glassy carbon and Ag/Ag+ (0.1 M AgNO3) were used as working and reference electrodes, respectively. The scan rate was maintained at 100 mV/s.

**Synthesis of Ligands.** 6-(1H-Imidazol-1-yl)-2,2′-bipyridine (bi): To a flask containing 6-bromo-2,2′-bipyridine (0.47 g, 2 mmol), imidazole (0.16 g, 2.4 mmol), potassium carbonate (0.33 g, 2.4 mmol) in dry acetonitrile, methyl iodide (0.13 mL, 2 mEq) was added. The solution was heated at 100 °C for 36 h. After the solution was cooled to room temperature, the solvent was removed under reduced pressure and extracted with CH2Cl2 (330 mL). The organic layer was washed with brine and dried with Na2SO4. Purification with silica gel column chromatography (DCM:MeOH = 20:1) gave white solid in 95% yield (0.43 g). 1H NMR (400 MHz, CDCl3) δ 8.67 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 8.45 (s, 1H), 8.40 (dt, J = 8.0, 1.0 Hz, 1H), 8.34 (dd, J = 7.8, 0.7 Hz, 1H), 7.89 (t, J = 7.9 Hz, 1H), 7.84–7.79 (m, 1H), 7.72 (t, J = 1.3 Hz, 1H), 7.34–7.30 (m, 2H), 7.23 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 155.5, 154.7, 149.1, 148.3, 139.9, 136.9, 134.9, 130.6, 124.2, 121.1, 118.9, 116.1, 111.9; HRMS (FAB+), m/z [M+H]+ found (calc): 223.0986 (223.0984). 3-[2,2′-Bipyridin]-6-yl-1-methyl-1H-imidazol-3-ium hexafluorophosphate (bim): To a flask containing bi (0.22 g, 1 mmol) in dry acetonitrile, methyl iodide (0.13 mL, 2 mEq) were subsequently distilled under nitrogen prior to use. Ethylene glycol (Aldrich) was used without further purification. Tetrakis(triphenylphosphine)- palladium(0) was purchased from Pressure Chemical Co.

**Experimental**

**Materials.** All reactions were carried out under a nitrogen atmosphere unless otherwise noted. Standard Schlenk techniques were employed to manipulate air-sensitive solvents, while workup procedures were done in air. Tetrahydrofuran (THF) were purchased from Fischer Scientific (HPLC grade) and dried over Na/benzophenone and were subsequently distilled under nitrogen prior to use. Toluene was purchased from Samchun Chemicals and dried over Na2SO4. Purification with silica gel column chromatography (DCM:MeOH = 95:5) gave white solid in 85% yield (0.23 g).

The presence of the NNC moiety is connected to bpy with or without a methylene bridge and thus lies at the corner of the tridentate ligand. Due to the presence of bpy moiety in both NNC- and NN′C-type ligands, a minimum conjugation is ensured at least up to two pyridyl rings. This structural motif prohibits an ultimate destabilization of the unoccupied MO energy level derived from the confined electronic delocalization in the single pyridyl ring observed in the big example.10(a) (2) The presence of the methylene bridge is manipulated to vary the strength of a ligand field induced by NHC moiety. With a methylene bridge, the Npyridine-Ru-Ccarbene bite angle becomes near orthogonal, thus inducing an augmented ligand field.8(a) (3) Employing a benzimidazolyl group in place of a simple imidazole one has multi purposes; one of which is to reduce the σ-donating power of the NHC moiety. And the last one is to increase the absorption intensity of the complex by increasing the light absorbing cross section.

During our analyses of experimental and theoretical calculation data of these series complexes, we found that λmax values are strongly correlated to electrochemical oxidation potentials (E1/22+/3+) rather than the commonly accepted HOMO-LUMO gaps. Here we report these results.
mmol) was added and heated reflux for 4 h. After the solution was cooled to room temperature, the solvent was removed by rotary evaporator. Crude mixture was dissolved with minimum amount of methanol and dropped to diethyl ether. White precipitate was filtered and redissolved in 10 mL of water. Excess NH₄PF₆ was added and the resulting solution was stirred for 10 min. White precipitate was filtered, washed with water and dried by vacuo (yield: quantitative). ¹H NMR (400 MHz, DMSO) δ 10.21 (s, 1H), 8.75 (d, J = 8.0 Hz, 1H), 8.65 (t, J = 2.0 Hz, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.53 (d, J = 8.0 Hz, 1H), 8.33 (t, J = 8.0 Hz, 1H), 8.04 (dt, J = 7.0, 2.0 Hz, 2H), 7.98 (t, J = 1.8 Hz, 1H), 7.55 (dd, J = 7.5, 4.8, 1.1 Hz, 1H), 4.01 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 155.0, 153.4, 149.7, 146.1, 141.9, 137.7, 135.8, 125.3, 124.9, 121.4, 121.2, 119.2, 113.9, 36.5; HRMS (FAB⁺), m/z [M⁺]+ found (calc): 237.1141 (237.1140).

1-[(2,2'-Bipyridin-6-yl)-1H-benzimidazol-3-ium Hexafluorophosphate (b'zim)]: The same procedure as the synthesis of b'zim. 6-(Chloromethyl)-2,2'-bipyridine (0.45 g, 2.2 mmol) and 1-methylbenzimidazole (0.16 g, 2.0 mmol) gave b'zim in quantitative yield. (0.892 g) ¹H NMR (400 MHz, DMSO) δ 9.95 (s, 1H), 8.66 (dd, J = 4.8, 1.8, 0.9 Hz, 1H), 8.35 (dd, J = 7.9, 0.9 Hz, 1H), 8.10–8.02 (m, 4H), 7.90–7.85 (m, 1H), 7.74–7.66 (m, 3H), 7.44 (dd, J = 7.5, 4.8, 1.2 Hz, 1H), 6.01 (s, 2H), 4.17 (d, J = 0.4 Hz, 3H). ¹³C NMR (100 MHz, DMSO) δ 155.2, 154.2, 152.8, 149.4, 143.6, 138.8, 137.4, 131.9, 131.3, 126.7, 126.5, 124.5, 122.9, 120.4, 120.2, 113.9, 113.7, 50.8, 33.4; HRMS (FAB⁺), m/z [M⁺]+ found (calc): 301.1455 (301.1453).

General Procedure for Ru Complexes.

Ru(tpy)L: Rut(pcy)Cl₃ (132 mg, 0.3 mmol) and L (0.3 mmol) in 5 mL of ethylene glycol was heated at 180 °C for 4 h. After the solution was cooled to room temperature, the solution was added dropwisely to saturated aqueous solution of NH₄PF₆, causing to precipitation of the compound. After the precipitate was filtered, it was purified by silica gel column chromatography (CH₂Cl₂:CN0.5 M NaN₃O₃ = 9:1).

Ru(tpy)(bim) (I): Orange solid; Yield: 59%. ¹H NMR (400 MHz, DMSO) δ 9.01 (s, 1H), 8.99 (s, 1H), 8.88–8.82 (m, 2H), 8.78 (s, 1H), 8.77 (s, 1H), 8.59 (d, J = 2.3 Hz, 1H), 8.55 (dd, J = 8.3, 1.1 Hz, 1H), 8.53–8.49 (m, 1H), 8.47 (t, J = 8.1 Hz, 1H), 8.07 (td, J = 7.9, 1.5 Hz, 1H), 8.02 (td, J = 7.9, 1.5 Hz, 2H), 7.52 (dd, J = 5.1, 1.0 Hz, 1H), 7.36 (dd, J = 5.6, 0.8 Hz, 2H), 7.32 (dd, J = 7.5, 5.5, 1.2 Hz, 1H), 7.28–7.22 (m, 3H), 2.76 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 184.5, 157.0, 155.2, 154.5, 154.4, 152.3, 151.9, 150.3, 138.7, 138.2, 137.6, 134.9, 134.9, 127.6, 124.5, 124.4, 123.8, 119.6, 118.5, 111.8, 34.9; HRMS (FAB⁺), m/z [M⁺][PF₆]⁻ found (calc): 716.0695 (716.0708); Anal. calcld for C₇₉H₇₂F₂₂N₄P₂Ru: C, 40.48; H, 2.69; N, 11.39. Found: C, 40.36; H, 2.82; N, 11.27.

Ru(tpy)(b'zim) (II): Light orange solid; Yield: 52%. ¹H NMR (400 MHz, CD₂CN) δ 8.72 (d, J = 8.2 Hz, 2H), 8.59 (dd, J = 17.0, 8.8 Hz, 3H), 8.48 (t, J = 8.2 Hz, 3H), 8.41 (t, J = 8.2 Hz, 1H), 8.25 (d, J = 8.2 Hz, 1H), 8.01 (td, J = 8.0, 1.5 Hz, 1H), 7.92 (td, J = 8.0, 1.4 Hz, 1H), 7.50 (t, J = 7.3 Hz, 1H), 7.42 (dd, J = 9.1, 6.5 Hz, 2H), 7.28 (dt, J = 7.4, 4.2 Hz, 4H), 7.16–7.09 (m, 2H), 2.98 (s, 3H). ¹³C NMR (75 MHz, CD₂CN) δ 199.7, 158.2, 156.5, 156.3, 155.9, 154.3, 135.5, 151.2, 139.9, 139.2, 138.8, 136.7, 136.4, 133.0, 128.5, 128.3, 125.7, 125.4, 125.4, 124.0, 118.0, 113.6, 112.3, 111.7, 33.4; HRMS (FAB⁺), m/z [M⁺][PF₆]⁻ found (calc): 766.0859 (766.0866); Anal. calcld for C₇₉H₇₂F₂₂N₄P₂Ru: C, 43.53; H, 2.77; N, 10.77; Found: C, 43.48; H, 2.89; N, 10.69.

Ru(tpy)(b''im) (III): Red solid; Yield: 56%. ¹H NMR (400 MHz, DMSO) δ 8.93 (t, J = 8.3 Hz, 3H), 8.72 (t, J = 8.3 Hz, 1H), 8.70 (t, J = 7.7 Hz, 2H), 7.73 (s, 2H), 7.67 (d, J = 7.5 Hz, 1H), 7.32–7.27 (m, 1H), 5.81 (s, 2H), 4.08 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 156.5, 154.9, 153.7, 149.8, 139.2, 137.8, 138.7, 125.0, 124.1, 123.7, 123.0, 121.0, 120.5, 53.4, 36.3; HRMS (FAB⁺), m/z [M⁺]+ found (calc): 251.1295 (251.1297).
Scheme 3. Synthesis of NNC ligands, bim and bzm.
ing acetonitrile gave b^im and b^zim, respectively, in quantitative yields.

Heteroleptic Ru complexes ([Ru(tpy)L]^{2+}) were synthesized by a reaction between [Ru(tpy)Cl3] and a slight excess amount of ligand L in a refluxing ethylene glycol solution for 4 h. For homoleptic Ru complexes (RuL^{2+}), RuCl3 and ligand L were heated as the same procedures of Ru(tpy)L. All complexes were obtained in moderate yields (52-71%). Meanwhile, other synthetic approaches, such as Ag(I) transmetalation also provided the target products, but yields were poor (ca. 15%).

Absorption Spectroscopy and Electrochemistry. Figure 1. displays electronic absorption spectra of seven complexes as well as their archetypal benchmark molecules, [Ru(bip)2]^{2+} and CTN for homoleptic and heteroleptic series, respectively. The corresponding \( \lambda_{\text{max}} \) and \( \varepsilon \) values are listed in Table 1. All complexes exhibit conventional absorption signatures characteristic of intense bands in the ultraviolet region (250-330 nm) for \( \pi-\pi^* \) ligand centered (LC) transitions and moderately intense bands in the visible region (400-600 nm) for metal-to-ligand charge transfer (MLCT) bands. Further examination using the time-dependent density functional theory (TD-DFT) confirms these attributions, except for the fact that a mixed-metal-ligand-to-ligand CT is more suitable for describing the latter case (Table S1).

The \( \lambda_{\text{max}} \) values in the lower energy region reside between 464-484 nm for the heteroleptic series and 455-494 nm for the homoleptic series. The \( \lambda_{\text{max}} \) values for the homoleptic series span wider than those for the homoleptic one, whose background will be discussed in the later part of this paper. Interestingly, the absorption signatures of these series complexes display clear trends as follow: (1) Complexes possessing NN^C-type ligand have lower energy \( \lambda_{\text{max}} \) values than those possessing NNC-type ligand. (2) Complexes possessing imidazole group in their respective NNC- or NN^C-type ligands have lower energy \( \lambda_{\text{max}} \) values than those possessing benzimidazolyl group. (3) Heteroleptic complexes have larger \( \varepsilon \) values compared to homoleptic counterparts. (4) Complexes possessing NN^C-type ligand have larger \( \varepsilon \) values relative to those possessing NNC-type ligand within the respective heteroleptic and homoleptic series. Trend (1) is contrary to our anticipation because if a conjugation is disrupted in NN^C-type ligand, the \( \lambda_{\text{max}} \) values would shift to the blue. This behaviour can be found in the literature by comparing two separate examples reported in ref. 7(a) and 8(a), respectively. In ref 7(b), \( \lambda_{\text{max}} \) of [Ru(tpy-CO2H)(CNC)]^{2+} (CTN) is 463 nm while that of [Ru(tpy)(C^N^C)]^{2+} in ref 8(a) is ~500 nm. Although a direct comparison might not be appropriate because of a presence of carboxylic acid group in the tpy ligand in CTN, these two systems roughly indicate that whether the extent of electronic delocalization includes NHC moiety is not a major factor in determining the \( \lambda_{\text{max}} \) of Ru(NHC) complexes. Trend (2) combined with the results described above regarding trend (1) indicate that \( \lambda_{\text{max}} \) values are more affected by the \( \sigma \)-donating power induced by NHC moiety. This analysis drives us to examine the relationship between \( \lambda_{\text{max}} \) and \( \sigma \)-donating power more closely. Since the magnitude of \( \sigma \)-donating power is best indicated by electrochemical redox potentials, we measured redox potentials of the series complexes and considered the dependence of these values on \( \lambda_{\text{max}} \).

Electrochemical oxidation potentials of the seven complexes in acetonitrile at 23 °C were recorded and their values are listed in Table 1. The one-electron reversible reductions of heteroleptic series occur within 0.05 V range (−1.02 ~ −1.07 V vs. NHE) while those of homoleptic ones do within 0.04 V range (−1.08 ~ −1.12 V vs. NHE). These confinements
Manipulation of Absorption Maxima by Controlling Oxidation Potentials


of reduction potentials originate the fact that LUMOs of these series are located either tpy or bpy ligand, both of which have very similar energy levels. We will show the shapes and energies of frontier orbitals of new complexes in the later part of this paper. On the contrary, the one-electron reversible oxidation potentials of complexes significantly differ each other according to the nature of the ligand. The values of heteroleptic series are 1.34, 1.45, 1.46, and 1.53 V vs. NHE for complexes 3, 4, 1, and 2, respectively. Those of homoleptic series are 1.15, 1.43, and 1.52 V vs. NHE for complexes 6, 7, and 5, respectively. The maximum difference of the values is ca. 0.2 V. The trend of oxidation potential values is similar to that of absorption maxima.

NN^C-type ligand gave more σ-donating effect than NNC-type one and the imidazole group provide more σ-donating effect than the benzimidazolyl group. As a result, HOMO-LUMO gaps of the series measured by electrochemical method are appeared to be dependent only on the oxidation potential values phenomenologically.

Figure 3 displays the relationship between the oxidation potential values and $\lambda_{\text{max}}$. As mentioned earlier, only $E_{1/2}^{2+/3+}$ values are strongly dependent on $\lambda_{\text{max}}$ yet $E_{1/2}^{1+/2+}$ values are essentially invariant with respect to $\lambda_{\text{max}}$ for both homoleptic and heteroleptic series. The degrees of correlation between $E_{1/2}^{2+/3+}$ and $\lambda_{\text{max}}$ values for both homoleptic and heteroleptic series are very similar to each other as manifested by the virtually same slopes of each trend line.

In general, $\lambda_{\text{max}}$ values scale with HOMO-LUMO gap; a gradual increase of $\lambda_{\text{max}}$ coincides with a concomitant destabilization of HOMO and a stabilization of LUMO. Therefore, a strong dependence of $E_{1/2}^{2+/3+}$ values on $\lambda_{\text{max}}$ is perhaps natural. The prominent dependence of $\lambda_{\text{max}}$ only on $E_{1/2}^{2+/3+}$ values is phenomenological behaviour embossed by the silent dependence of $\lambda_{\text{max}}$ values on $E_{1/2}^{1+/2+}$ ones. The background of levelling effect of $E_{1/2}^{1+/2+}$ values can be rationalized as follow: (1) In the heteroleptic series, most of

Table 1. Spectroscopic and voltammetric data

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ ($\times 10^4$)</th>
<th>$E_{1/2}^{2+/3+}$ (V)</th>
<th>$E_{1/2}^{1+/2+, 0T1+, a}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ru(tpy)(bim)</td>
<td>470</td>
<td>1.14</td>
<td>1.46</td>
<td>-1.07, -1.34</td>
</tr>
<tr>
<td>2. Ru(tpy)(bzim)</td>
<td>464</td>
<td>1.20</td>
<td>1.53</td>
<td>-1.04, -1.35</td>
</tr>
<tr>
<td>3. Ru(tpy)(b^im)</td>
<td>484</td>
<td>1.26</td>
<td>1.34</td>
<td>-1.06, -1.33</td>
</tr>
<tr>
<td>4. Ru(tpy)(b^zim)</td>
<td>477</td>
<td>1.23</td>
<td>1.45</td>
<td>-1.02, -1.30</td>
</tr>
<tr>
<td>5. Ru(bim)$_2$</td>
<td>466</td>
<td>0.85</td>
<td>1.43</td>
<td>-1.12, -1.36</td>
</tr>
<tr>
<td>6. Ru(bzim)$_2$</td>
<td>455</td>
<td>0.84</td>
<td>1.52</td>
<td>-1.08, -1.35</td>
</tr>
<tr>
<td>7. Ru(b^im)$_2$</td>
<td>495</td>
<td>1.01</td>
<td>1.15</td>
<td>-1.08, -1.45</td>
</tr>
<tr>
<td>[Ru(bip)$_2$]$_2^2+$</td>
<td>382</td>
<td>1.52</td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td>[Ru(tpy)$_2$]$_2^2+$</td>
<td>474</td>
<td>1.72</td>
<td>1.55</td>
<td>-0.99</td>
</tr>
</tbody>
</table>

$^a$Experimental conditions: [compound] = 5 mM; [TBAPF$_6$] = 0.1 M; solvent = acetonitrile; temperature = 25 ± 1 °C; scan rate = 100 mV/s; reference electrode = Ag/Ag$^+$; working electrode = glassy carbon. All potentials are referenced to a ferrocene/ferrocenium redox couple as an internal standard and converted to NHE by the relation ferrocene/ferrocenium vs. NHE = +0.64 V. $^b$From ref. 7(a).

Figure 2. Cyclic voltammogram of seven complexes. Gradual shift of oxidation potential is guided by red dot line. Invariant reduction potential is guided by blue dot line. Experimental conditions: [compound] = 5 mM; [TBAPF$_6$] = 0.1 M; solvent = acetonitrile; temperature = 23 °C; scan rate = 100 mV/s; reference electrode = Ag/Ag$^+$; working electrode = glassy carbon. All potentials are referenced to a ferrocene/ferrocenium redox couple as an internal standard and converted to NHE by the relation ferrocene/ferrocenium vs. NHE = +0.64 V.
the electronic population in LUMO is localized at tpy ligand regardless of a second ligand. The LUMO energy is primarily determined by the tpy energy level, which is not affected by Ru(NNC) or Ru(NN^C) moiety. (2) In the homoleptic series, most of the electronic population in LUMO is localized at bpy moiety of one of two NNC-type ligands (5) or equally at two bpy moieties of each ligand (6 and 7). As a result, the LUMO energies of each series are levelled. The absolute level of trend line of the $E_{\text{LUMO}}$ dependencies for a homoleptic series is slightly higher than that for a heteroleptic one. This pattern mirrors the LUMO energies of bpy and tpy of their own, which are determined by DFT calculation. While the slopes of two trend lines of both homoleptic and heteroleptic series are virtually the same, the absolute levels of those two differ by 0.1 V; it is quite natural that the destabilization of HOMO with two NHC ligands is more pronounced than that with only one unit.

The significant destabilization of HOMO level in homoleptic [Ru(b^im)2]$^{2+}$ is worth noting. Considering the fact that the oxidation potential of [Ru(bip)2]$^{2+}$ in which four NHC moieties are coordinated to the Ru center is only 1.38 V, an observed value of 1.15 V [Ru(b^im)]$^{2+}$ is remarkable. Due to this substantial negative shift of oxidation potential, $\lambda_{\text{max}}$ values of [Ru(b^im)2]$^{2+}$ exhibit substantial bathochromic shift up to 495 nm, thus causing widely spread $\lambda_{\text{max}}$ values of homoleptic series.

**Computational Study.** The geometry optimizations and electronic structure calculations of seven new complexes were performed via using density functional theory (DFT). The nature of each MO is characterized by percent contribution of each atom summed into several classes; Ru, tpy, bpy, and imidazolyl or benzimidazolyl part for heteroleptic series, and Ru, bpy, and imidazolyl or benzimidazolyl part for homoleptic series (Table 2). The 3-dimensional represent-

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**Table 2. Energies and Percent Compositions of Frontier MOs of Ru(tpy)L and RuL$_2$**

<table>
<thead>
<tr>
<th>MO</th>
<th>Electron Population (%)</th>
</tr>
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<tbody>
<tr>
<td>1. Ru(tpy)(bim)</td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>E (eV)</td>
</tr>
<tr>
<td>----</td>
<td>------</td>
</tr>
<tr>
<td>3$^d$</td>
<td>-2.43</td>
</tr>
<tr>
<td>2$^d$</td>
<td>-2.53</td>
</tr>
<tr>
<td>1$^d$</td>
<td>-2.60</td>
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*Methylimidazole part of ligand.*
*Methylbenzimidazole part of ligand.*
*Bipyridyl part of NNC or NN^C ligand.*

$^a$ and $^b$ denote HOMO-1, HOMO-2, HOMO-3, respectively while $^c$ denote LUMO+1 and LUMO+2, respectively.
tations of the isosurfaces of each MO clearly confirm the character of the MO (Figure 4). For all seven complexes, the three highest occupied orbitals of these complexes have their majority of electron populations (56-84%) at Ru metal while three lowest unoccupied MOs have those in tpy or bpy ligands indicating that the lowest energy absorption bands are metal-to-ligand charge transfer in character. It is important to note that substantial amount of the electron population of HOMO is delocalized over azolyl ring plane (18-30%) highlighting the significant contribution of NHC group to the shape and energy of the HOMO. The degree of \( \sigma \)-donation can be modulated by the type of NHC ligands as well as their geometries. Complexes with NN\(^{\text{C}}\)-type ligand have geometries more close to the perfect octahedron in terms of N-Ru-C bite angle compared to those with NNC-type one.\(^{8(a)}\) For heteroleptic series, the ligand field applied by the NHC moiety is thus more prominent in complex 3 and 4 than in complex 1 and 2. Accordingly, the degree of destabilization of HOMO energy level is thus more prevailing in complex 3 and 4. The same is true for the homoleptic series; complex 7 has higher HOMO energy level compared to complex 5 and 6. When we focus on the nature of NHC ligand, imidazolyl group provide stronger ligand field than benzimidazolyl group since the electronic populations are far more delocalized over the aromatic ring in benzimidazolyl ring, thus weaken the \( \sigma \)-donating effect. As a result, the energy levels of HOMOs with benzimidazolyl group are less destabilized compared to those with simple imidazolyl group. These analyses clearly show how the structure and geometry NHC moiety affect the shapes and energies of HOMOs.

As shown in Figure 4, the electronic populations in the LUMOs of heteroleptic series are apparently localized in the whole tpy ligand, while those of homoleptic series are separately localized in the two bpy ligands. As mentioned earlier, the energy levels of LUMOs of tpy or bpy are similar each other. No matter what the LUMO is localized in one tpy ligand or two bpy ones, the resulting reduction potentials of such complexes are thus appear to be similar. In the case of HOMOs, however, electronic populations are shared by Ru metal and NHC moiety of NNC or NN\(^{\text{C}}\)-type ligands.

The energies of the frontier MOs are compared in Figure 5 along with those of [Ru(tpy)\(_2\)]\(^{2+}\) and [Ru(bip)\(_2\)]\(^{2+}\) benchmarks. The calculation results are in excellent agreement with the experimental electrochemical data as well as the absorption spectroscopic data highlighted by the red dotted guide lines.

**Conclusion**

In sum, we have newly synthesized seven Ru complexes...
that possess a heteroleptic [Ru(tpy)(NHC)]^{2+} or a homo-
leptic [Ru(NHC)]^{2+} topology and feature NNC- or NN^C-
type NHC structural motif. These complexes have varying
degrees of oxidation potentials induced by different ligand
field of NHC moiety, yet have levelled reduction potential
due to the similar LUMO energy localized in bpy or tpy
moiety. We observed that the \( \lambda_{\text{max}} \) values of these series
complexes are correlated with only the oxidation potentials.
Given the structure-property relationship obtained in this
study, we could modulate \( \lambda_{\text{max}} \) values of Ru(NHC) complexes
to some extent.

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