

## Synthesis, Crystal Structure, and Optical and Photoelectrochemical Properties of a $N \cap O^-$ Rhenium(I) Complex

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The neutral dimer complex  $\text{Re}_2(\text{CO})_6(\text{BIZ})_2$  was directly obtained from a simple reaction between Re(CO)<sub>5</sub>Cl and N∩OH-type ligand 2-(1-phenyl-1*H*-benzoimidazol-2-yl)phenol (HBIZ). The further reaction of Re<sub>2</sub>(CO)<sub>6</sub>(BIZ)<sub>2</sub> with pyridine (Py) led to the monomeric Re(CO)<sub>3</sub>(BIZ)(Py), which was characterized by means of single-crystal X-ray diffraction analysis, <sup>1</sup>H NMR, elemental analysis, and UV-visible absorption, photoluminescence, and infrared spectroscopy as well as cyclic voltammetry. The photoelectrochemical properties of Re(CO)<sub>3</sub>(BIZ)(Py) spin-coated film modified indium-tin oxide electrode were investigated, and a large cathodic photocurrent up to  $0.55 \,\mu\text{A/cm}^2$  at -0.3 V bias potential was observed. The LUMO and HOMO energy levels of Re(CO)<sub>3</sub>(BIZ)(Py) were studied by density functional theory calculations. The possible mechanism of the photocurrent generation was discussed.

## Introduction

In recent decades, the Re(I) diimine carbonyl complexes have attracted considerable attention due to their intriguing photophysical, photochemical, and electrochemical properties.<sup>1-3</sup> They also have excellent potential applications in molecular and supramolecular luminescence sensing and switching devices,<sup>1</sup> probes of environmental changes,<sup>4</sup> electroluminescence,<sup>5–8</sup> photocatalysis,<sup>9</sup> and therapeutic radiopharmaceuticals.<sup>10</sup> Among the Re(I) complexes reported, the  $Re(CO)_3^+$  complexes of general formula  $Re(CO)_3(N \cap N)X$  (where  $X = Cl^-$ , Br<sup>-</sup>, I<sup>-</sup>, or a neutral ligand such as acetonitrile or pyridine) with  $N \cap N$  aromatic diamine bidentate neutral ligands have

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been heavily studied.<sup>11-14</sup> In contrast, the  $Re(CO)_3^+$  complexes containing the anionic  $N \cap C^-$ ,  $N \cap S^-$ , and  $N \cap O^$ bidentate ligands have received little attention; particularly, their photoelectric properties have been ill explored.<sup>15–23</sup> We have previously reported electroluminescent properties of a complex of this family.<sup>21</sup> In order to continue our efforts on  $\operatorname{Re}(\operatorname{CO})_3(N \cap N)(X)^{-5}$  and  $\operatorname{Re}(\operatorname{CO})_3(N \cap O^{-})(X)^{21}$ -type  $\operatorname{Re}(I)$ complexes, we have synthesized, structurally characterized, and photoelectrochemically studied a new Re(I) complex,  $Re(CO)_3(BIZ)(Py)$ , with N $\cap O^-$ -type ligand BIZ {BIZ = deprotonated 2-(1-phenyl-1*H*-benzoimidazol-2-yl)phenol}.

## **Experimental Section**

Materials and Apparatus. The synthesis of the target Re(I) complex is given as follows, and the other materials and instrumentation details are given in the Supporting Information.

Synthesis of 2-(1-Phenyl-1H-benzoimidazol-2-yl)phenol, HBIZ. A solution of N-phenylbenzene-1,2-diamine (0.92 g, 5 mmol) and 2-hydroxybenzaldehyde (0.61 g, 5 mmol) in 2-(2-methoxvethoxy)ethanol (10 mL) was microwave heated at 160 °C for 3 h

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under N<sub>2</sub>.<sup>24</sup> Upon cooling to room temperature, the reaction mixture was poured into water (200 mL). The precipitation formed was purified by column chromatography on silica gel using dichloromethane as eluent. The crude product obtained was recrystallized from hexane-dichloromethane (v/v = 1:1), affording 0.35 g of white crystals (25% yield).

Synthesis of  $\text{Re}_2(\text{CO})_6(\text{BIZ})_2$ . A solution of  $\text{Re}(\text{CO})_5\text{Cl}(0.10 \text{ g}, 0.28 \text{ mmol})$  and HBIZ (0.08 g, 0.28 mmol) in toluene (10 mL) was refluxed for 6 h under N<sub>2</sub>. The solid, precipitated upon cooling the solution to room temperature, was filtered, washed with dichloromethane, and dried at 100 °C in vacuo to obtain a white powder (0.12 g, 78% yield), which was directly used for the following synthesis without further purification due to solubility problems. Anal. Calcd for C<sub>44</sub>H<sub>26</sub>N<sub>4</sub>O<sub>8</sub>Re<sub>2</sub>: C 47.56, H 2.36, N 5.04. Found: C 48.20, H 2.40, N 4.64.

Synthesis of Re(CO)<sub>3</sub>(BIZ)(Py) (Py = pyridine). A suspension of Re<sub>2</sub>(CO)<sub>6</sub>(BIZ)<sub>2</sub> (0.12 g, 0.11 mmol) in pyridine (5 mL) was refluxed at 120 °C for 3 h under N<sub>2</sub>. The orange solid obtained after the solvent was removed under reduced pressure was recrystallized from hexane-dichloromethane (v/v = 1:1) to afford 0.11 g of yellow crystals (85% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  (ppm): 8.74 (d, 2H, *J* = 5.1), 7.90 (d, 1H, *J* = 8.2), 7.69 (t, 1H, *J* = 7.6), 7.54 (m, 3H), 7.34 (t, 1H, *J* = 7.7), 7.27 (m, 3H), 7.18 (m, 3H), 7.12 (t, 1H, *J* = 7.0), 6.97 (d, 1H, *J* = 7.9), 6.55 (d, 1H, *J* = 7.9), 6.15 (t, 1H, *J* = 7.1). Anal. Calcd for C<sub>27</sub>H<sub>18</sub>N<sub>3</sub>O<sub>4</sub>Re: C 51.09, H 2.86, N 6.62. Found: C 51.17, H 2.94, N 6.64.

## **Results and Discussion**

Re(CO)<sub>3</sub>(BIZ)(Py) was synthesized according to the route described in Scheme S1 (Supporting Information) and was characterized by elemental analysis, <sup>1</sup>H NMR spectroscopy, and single-crystal X-ray diffraction. As shown by thermogravimetric and differential thermal curves (see Figures S1 and S2, Supporting Information), Re<sub>2</sub>(CO)<sub>6</sub>(BIZ)<sub>2</sub> and Re(CO)<sub>3</sub>(BIZ)-(Py) did not melt before they started thermal decomposition at 418 and 218 °C, respectively.

The crystals of Re(CO)<sub>3</sub>(BIZ)(Py) suitable for single-crystal X-ray analysis were obtained by slow evaporation of a hexanedichloromethane (v/v = 1:1) solution. A perspective drawing of the structure of Re(CO)<sub>3</sub>(BIZ)(Py) with atomic numbering scheme is shown in Figure 1, and the crystallographic data are given in Table S1 in the Supporting Information. Selected bond lengths and angles for Re(CO)<sub>3</sub>(BIZ)(Py) are shown in Tables S2 and S3 (Supporting Information), respectively. The bond length of Re–N<sub>chel</sub> (from the N $\cap$ O<sup>-</sup> ligand, 2.177 Å) is shorter than that of  $Re-N_{pyr}$  (from pyridine, 2.217 Å), revealing that the  $N_{chel}$  atom binds to Re more strongly than the  $N_{pyr}$  atom. The bond length of Re-O<sub>chel</sub> (2.125 Å) is shorter than that of Re–N<sub>chel</sub> (2.177 Å), indicating stronger coordination ability of O<sub>chel</sub> than that of N<sub>chel</sub> and the covalent character of the Re– $N_{pyr}$  and Re– $N_{chel}$  bonds.<sup>25–27</sup> The bond lengths of Re– $O_{chel}$  (2.125 Å) and C– $O_{chel}$  (1.326 Å) support the ionic character of the Ochel atom, and accordingly the enol character of the ligand. The bond length of Re-O<sub>chel</sub> in Re(CO)<sub>3</sub>(BIZ)(Py) is close to that previously reported in Re- $(CO)_3(BIP)(Py)^{20}$  {BIP = deprotonated 2-(1-methyl-1*H*-benzoimidazol-2-yl)phenol} within experimental error, while the bond length of Re-N<sub>chel</sub> (2.177 Å) in Re(CO)<sub>3</sub>(BIZ)(Py) is longer than that (2.155 Å) in Re(CO)<sub>3</sub>(BIP)(Py). It can also be seen that there is less steric hindrance for pyridine coordination

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Figure 1. Perspective drawing of  $Re(CO)_3(BIZ)(Py)$  with atomic numbering scheme. Thermal ellipsoids are shown at the 30% probability level.

in Re(CO)<sub>3</sub>(BIZ)(Py) than in Re(CO)<sub>3</sub>(BIP)(Py), namely, N<sub>pvr</sub> more strongly binds to Re in Re(CO)<sub>3</sub>(BIZ)(Py) than in Re- $(CO)_3(BIP)(Py)$ , as illustrated by the shorter bond length of  $Re-N_{pvr}$  (2.217 Å) in  $Re(CO)_3(BIZ)(Py)$  than that (2.230 Å) in Re(CO)<sub>3</sub>(BIP)(Py). Selected bond angles of Re(CO)<sub>3</sub>(BIZ)(Py) (see Table S3) clearly indicate that the CO ligands are linearly coordinated; C22, C21, O1, N1, Re1 as well as C22, C20, O1, N3, Re1 are coplanar. In other words, the pyridine ring coordinated via its N atom to Re is nearly perpendicular to the plane consisting of C22, C21, O1, N1, and Re1. The bond angle of C(1)-O(1)-Re(1) is found to be 117.7°, characteristic of an  $sp^3$  hybrid state of O(1). The bond angles between adjacent CO {C(20)-Re(1)-C(21), C(22)-Re(1)-C(20), C-(22)-Re(1)-C(21) are 87.6-89.1°, which are close to 90°, but the bond angle between the coordinated nitrogen and oxygen atom in ligand BIZ,  $\{O(1) - Re(1) - N(1)\}$ , is 80.41°, which is much less than 90°, due not only to the steric requirement of the bidentate ligand BIZ but also to a twist of the imidazole ring relative to the phenol plane. This twist is clearly verified by the dihedral angle ( $\sim$ 32°) between the imidazole and the phenol rings.

The IR spectrum of Re(CO)<sub>3</sub>(BIZ)(Py) (see Figure S3, Supporting Information) exhibited two distinct  $\nu_{CO}$  bands in the region of CO stretching vibration (1800–2100 cm<sup>-1</sup>), which are different from three  $\nu_{CO}$  bands observed for Re<sub>2</sub>-(CO)<sub>6</sub>(BIZ)<sub>2</sub> and previously reported pseudooctahedral Re(I) complexes with three facial CO ligands.<sup>21,22,28</sup> This could be understood by the fact that two of three C–Re bond lengths {1.901(3), 1.900(3), and 1.916(3) Å} as well as two of three C–O bond lengths {1.153(4), 1.148(3), and 1.158(3) Å} in Re(CO)<sub>3</sub>(BIZ)(Py) are almost the same within experimental errors.

 $Re(CO)_3(BIZ)(Py)$  is well soluble in a wide range of organic solvents, polar and less polar as well. On the contrary, dimeric  $Re_2(CO)_6(BIZ)_2$  is much less soluble in organic solvents than the monomeric  $Re(CO)_3(BIZ)(Py)$ .  $Re_2(CO)_6(BIZ)_2$  is not stable in strongly coordinating solvents with relatively high values of the donor number DN, such as pyridine, nitriles, and amides,<sup>29,30</sup> dissociating into  $Re(CO)_3(BIZ)(solv)$ . However, it

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**Figure 2.** Evolution of UV–visible absorption spectra of  $10 \,\mu$ M Re<sub>2</sub>(CO)<sub>6</sub>(BIZ)<sub>2</sub> in pyridine with time (from 0 to 250 min). Arrow shows spectral changes upon increasing time.

is stable toward weakly coordinating solvents such as dichloromethane and toluene, similar to analogous  $N \cap O^-$  Re(I) complexes.<sup>20</sup> The UV-vis absorption spectra of Re<sub>2</sub>(CO)<sub>6</sub>-(BIZ)<sub>2</sub> and Re(CO)<sub>3</sub>(BIZ)(Py) in dichloromethane are compared in Figure S4 (Supporting Information). Re<sub>2</sub>(CO)<sub>6</sub>(BIZ)<sub>2</sub> exhibited a metal-to-ligand charge-transfer (MLCT) absorption band (shoulder) centered at around 330 nm and a  $N \cap O^$ ligand-based  $\pi - \pi^*$  absorption band centered at 295 nm, which was red-shifted by 10 nm and blue-shifted by 15 nm, respectively, relative to  $\text{Re}_2(\text{CO})_6(\text{TOB})_2^{21}$  {TOB = deprotonated 2-(2H-benzo[d][1,2,3]triazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol} and  $\text{Re}_2(\text{CO})_6(\text{BIP})_2$  in the same solvent.<sup>22</sup> Re(CO)<sub>3</sub>(BIZ)(Py) in dichloromethane showed a strong well-defined absorption band at 295 nm that is almost the same as that observed for the dimer, and a low-energy band centered at 380 nm that is close to that previously reported for structurally similar Re(CO)<sub>3</sub>(BIP)(Py)<sup>22</sup> and blue-shifted by 40 nm compared with Re(CO)<sub>3</sub>(TOB)(Py).<sup>21</sup> The evident difference in the UV-vis absorption spectra between the monomeric and dimeric complexes can be utilized to monitor their presence in solution. In particular the absorbance above 350 nm may serve as a fingerprint of the monomeric form. In this region,  $Re_2(CO)_6(BIZ)_2$  is almost transparent, whereas Re(CO)<sub>3</sub>(BIZ)(Py) shows intense absorption; thus we can monitor the spectral evolution of  $Re_2(CO)_6(BIZ)_2$  with time in a coordinating medium. The time-dependent spectral changes of Re<sub>2</sub>(CO)<sub>6</sub>(BIZ)<sub>2</sub> in neat pyridine are shown in Figure 2. The data were analyzed according to pseudo-first-order rate eq 1:<sup>19-21</sup>

$$A_t/A_{\infty} = 1 - \exp(-k_{\text{solv}}C_{\text{solv}}t)$$
(1)

where  $k_{\text{solv}}$  is the solvolysis rate constant, and  $A_t$  and  $A_{\infty}$  are the absorbance of the solution at time *t* and at the end of the reaction, respectively. If a highly excessive coordinating agent is applied, coordinating agent concentration  $C_{\text{solv}}$  at a given *t* stays approximately constant. On the basis of the data shown in Figure 2, a solvolysis rate constant  $k_{\text{solv}}$  is derived to be  $(3.9 \pm 0.1) \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1}$  for Re<sub>2</sub>(CO)<sub>6</sub>(BIZ)<sub>2</sub> in pyridine, is much lower than  $3.8 \times 10^{-1} \text{ M}^{-1} \text{ min}^{-1}$  previously reported

for  $\text{Re}_2(\text{CO})_6(8\text{-quinolinato})_2$  in pyridine-dichloromethane mixture,<sup>19</sup> and is the same order of magnitude as  $k_{solv}$  values of  $3.4 \times 10^{-3}$  and  $4.5 \times 10^{-3}$  M<sup>-1</sup> min<sup>-1</sup> previously reported for  $\operatorname{Re}_2(\operatorname{CO})_6(\operatorname{BOP})_2$  {BOP = deprotonated 2-benzoxazol-2-ylphenol} in pyridine-dichloromethane mixture<sup>20</sup> and  $Re_2(CO)_6(TOB)_2$  in neat pyridine,<sup>21</sup> respectively. However, it is much greater than  $k_{solv}$  values of  $3.3 \times 10^{-5}$  and  $1.1 \times 10^{-4}$ M<sup>-1</sup> min<sup>-1</sup> previously reported for Re<sub>2</sub>(CO)<sub>6</sub>(BIP)<sub>2</sub> and  $Re_2(CO)_6(BTP)_2$  {BTP = deprotonated 2-benzothiazol-2-ylphenol} in neat pyridine, respectively.<sup>20</sup> The intrinsic charac-teristics of different complexes may be the cause of the difference in the  $k_{solv}$  values. Re<sub>2</sub>(CO)<sub>6</sub>(BIZ)<sub>2</sub> and Re<sub>2</sub>(CO)<sub>6</sub>- $(BIP)_2$  differ only in methyl and phenyl substitutes, but the  $k_{solv}$ value of  $\text{Re}_2(\text{CO})_6(\text{BIZ})_2$  is 2 orders of magnitude greater than that of  $\text{Re}_2(\text{CO})_6(\text{BIP})_2$ . This may be because the planar phenyl in Re<sub>2</sub>(CO)<sub>6</sub>(BIZ)<sub>2</sub> has less steric hindrance to pyridine attack than the tetrahedral methyl in  $\text{Re}_2(\text{CO})_6(\text{BIP})_2$ .

The photoluminescence excitation and emission spectra of Re(CO)<sub>3</sub>(BIZ)(Py) in dichloromethane solution are shown in Figure S5 (Supporting Information). The excitation spectrum  $(\lambda_{em} = 510 \text{ nm})$  showed two distinct bands at 295 and 380 nm, which are close to the UV-vis absorption maxima. Upon excitation at both 295 and 380 nm, Re(CO)<sub>3</sub>(BIZ)(Py) exhibited a broad emission band centered at 510 nm from metal-toligand charge-transfer (<sup>3</sup>MLCT) excited state, <sup>19-21</sup> which is evidently different from two emission bands at 405 and 480 nm observed for the free HBIZ in the same solvent ( $\lambda_{ex} = 320 \text{ nm}$ ) and is blue-shifted by ~130 nm with respect to Re(CO)3-(TOB)(Py),<sup>21</sup> probably due to the better electron-donating property of BIZ than TOB. The photoluminescence quantum yield for Re(CO)<sub>3</sub>(BIZ)(Py) in air-saturated dichloromethane solution was determined to be 0.14% ( $\lambda_{ex} = 294 \text{ nm}$ ) and 0.2% ( $\lambda_{ex} = 380$  nm), and 0.16% ( $\lambda_{ex} = 294$  nm) and 0.23% ( $\lambda_{ex} =$ 380 nm) for N2-degassed dichloromethane solution, which are much lower than 2.1-3.2% previously reported for monomeric  $\text{Re}(\text{CO})_3(\text{L})(\text{Py})$  (in which L = BIP, BOP, and BTP)<sup>22</sup> and even lower than 0.36% for  $Re(CO)_3(TOB)(Py)^{21}$  in the same solvent. On the contrary, dimeric  $Re_2(CO)_6(BIZ)_2$  was too weakly emissive to be detected, similar to previously reported  $\text{Re}_2(\text{CO})_6(\text{BIP})_2$ .<sup>20</sup> The excited-state relaxation data at 510 nm for Re(CO)<sub>3</sub>(BIZ)(Py) in air-saturated dichloromethane were well fit to a single-exponential emission decay lifetime of 126.9  $\pm$  1.9 ns (see Figure S6, Supporting Information). Assuming an intersystem crossing yield of unity,<sup>31</sup> radiative  $(k_r)$  and nonradiative  $(k_{nr})$  rate constants were calculated to be  $k_r = 1.1 \times 10^4 \text{ s}^{-1}$  and  $k_{nr} = 7.9 \times 10^6 \text{ s}^{-1}$ .

Cyclic voltammograms (see Figure 3) of Re(CO)<sub>3</sub>(BIZ)(Py) exhibited two irreversible BIZ-based reduction waves at  $E_{\rm pc} = -2.18$  and -2.68 V with an onset reduction potential of -2.04 V and one irreversible oxidation wave at  $E_{1/2} = +1.10$  V with an onset oxidation potential of +0.96 V, which is assigned to a metal-based Re<sup>II</sup>/Re<sup>I</sup> oxidation process and is close to an  $E_{1/2}$  value of +1.20 V we previously reported for Re(CO)<sub>3</sub>(TOB)(Py).<sup>21</sup> The ligand HBIZ exhibited two couples of irreversible reduction waves at  $E_{1/2} = -1.27$  and -1.72 V vs SCE (see Figure S7, Supporting Information), which is less negative than those observed for the BIZ-based reduction in Re(CO)<sub>3</sub>(BIZ)(Py), indicating that BIZ in Re(CO)<sub>3</sub>(BIZ)(Py) is more difficult to reduce than in the free HBIZ. Unfortunately, the cyclic voltammetry of Re<sub>2</sub>(CO)<sub>6</sub>(BIZ)<sub>2</sub> could not be accomplished due to the solubility problem. From the onset

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Figure 3. Dependence of the cyclic voltammograms of Re-(CO)<sub>3</sub>(BIZ)(Py) in acetonitrile on the scan rates. The inset is the dependence of anodic peak currents for the oxidation wave at +1.19 V on the square root of scan rates.

anodic peak potential for oxidation process  $[E_{pa}(onset)]^{ox}$ and onset cathodic peak potential for reduction process  $[E_{pc}(onset)]^{red}$ , the HOMO and LUMO energy levels of Re-(CO)<sub>3</sub>(BIZ)(Py) were estimated by taking 4.74 eV for SCE with respect to the vacuum level according to the formulas  $E_{\rm HOMO} = -4.74 - [E_{\rm pa}({\rm onset})]^{\rm ox}, E_{\rm LUMO} = -4.74 [E_{pc}(\text{onset})]^{\text{red}}$ , and  $E_{LUMO} - E_{HOMO}$  in  $eV = 1240/\lambda_{max}$ , where  $\lambda_{\text{max}}$  is the wavelength in nm at which the material has the lowest-energy onset absorption.<sup>5,21,32-34</sup> These calculations give the HOMO and LUMO energy levels of -5.70and -2.70 eV, respectively. The gap between the LUMO and HOMO energy levels is thus derived to be 3.00 eV, which is about 0.05 eV greater than the value of 2.95 eV obtained from an absorption edge at 421 nm of visible absorption spectrum for Re(CO)<sub>3</sub>(BIZ)(Py) in CH<sub>2</sub>Cl<sub>2</sub> and is greater than a gap value of 2.65 eV we previously reported for Re(CO)<sub>3</sub>(TOB)-(Py).<sup>21</sup> The inset of Figure 3 shows a linear dependence of the anodic peak currents for the oxidation wave of Re(CO)3(BIZ)-(Py) at +1.19 V on the square root of scan rates, indicating diffusion-controlled redox reactions.35-37

The energies of some frontier molecular orbitals of Re-(CO)<sub>3</sub>(BIZ)(Py) were also computed using the density functional theory (DFT) method, and the results are shown in Figure S8 (Supporting Information). As shown in Table S3 (Supporting Information), the computed bond lengths and angles for Re(CO)<sub>3</sub>(BIZ)(Py) are very close to those structurally determined, indicating that the results of the geometry optimization by the DFT method are reliable. It can be seen that the highest occupied molecular orbital (HOMO) of Re-(CO)<sub>3</sub>(BIZ)(Py) is localized over the center metal atom (Re) and phenolic and carbonyl groups and the lowest unoccupied molecular orbital (LUMO) on the pyridine, indicating that the HOMO-LUMO excitation could move the electron distribution from the center Re atom to the pyridine unit. The LUMO and HOMO energies of the complex were computed to be -1.95 and -5.40 eV, respectively, giving a gap of 3.45 eV between the these two energy levels, which is greater than those (2.95-3.0 eV) obtained from the cyclic voltammetry and the visible absorption spectrum. This difference between the experimental and the calculated energy values is in good agreement with the error reported as a constant for transition metal complexes, which may be attributed to a systemic error coming from theory calculations and environment factors, e.g., molecular solvation, geometrical changes, and polarization in aqueous solution and so on.<sup>38,39</sup> Moreover, such a systemic error can be obviously reduced by using a standard sample correlation method, e.g.,  $[Ru(bpy)_3]^{2+}$  for Ru(II) complexes.40,41

Re(CO)<sub>3</sub>(BIZ)(Py) was also spin-coated from its dichloromethane solution onto ITO substrates for photoelectrochemical studies. The concentrations of the dichloromethane solutions were varied to prepare a Re(CO)<sub>3</sub>(BIZ)(Py)-modified ITO electrode of varied thickness. As shown in Figure S9 (Supporting Information), the absorbances at 380 nm or the film thicknesses of the Re(CO)<sub>3</sub>(BIZ)(Py) films increased linearly with increasing concentrations of the spin-coating solutions. As seen from Figure S10 (Supporting Information), the photocurrents attained saturation for a film prepared at a spin-coating solution concentration of 4 mg/mL and then decayed as the concentrations were further increased. This photocurrent trend is independent of the applied potentials. A 4 mg/mL concentration of the spin-coating solution was thus selected for making a spin-coating film for the photoelectrochemical studies described below. The film that was spincoated at this concentration showed relatively continuous island-like clusters or aggregates that were closely packed and randomly stacked, making the film rough and jagged at the surface, as revealed by scanning electron microscopy (see Figure S11, Supporting Information). The photoresponses of the Re(CO)<sub>3</sub>(BIZ)(Py) film on the ITO electrode under whitelight irradiation (100 mW/cm<sup>2</sup>) at different bias potentials are shown in Figure 4. As the negative bias potentials were applied to the working electrode, stable and rapid cathodic photocurrents were induced by switching on the irradiation to a Re(CO)<sub>3</sub>(BIZ)(Py) film. A photocurrent density up to  $0.55 \ \mu A/cm^2$  at -0.3 V bias potential was obtained. The photocurrent generation is prompt and reproducible with negligible decay under many on/off cycles of irradiation. As shown in Figure S12 (Supporting Information), the photocurrents increased as the applied bias potential becomes more negative, indicating that the photocurrent polarity is cathodic. In other words, the negative bias potential speeded up the generation of photoinduced electron-hole pairs in transferring the conduction band electron of ITO to the HOMO of  $Re(CO)_3(BIZ)(Py)$  and then to the electron acceptor in the supporting electrolyte, inhibiting the recombination of electronhole pairs. There is another possible reason that the bias potential on the electrode would increase the energy of the conduction band of ITO, making the electron transfer from the conduction band of ITO to the HOMO of Re(CO)<sub>3</sub>(BIZ)(Py)

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Figure 4. Current changes induced by switching on and off the white-light irradiation  $(100 \text{ mW/cm}^2)$  of the Re(CO)<sub>3</sub>(BIZ)(Py) film  $(0.28 \text{ cm}^2)$  at different bias potentials vs SCE. Supporting electrolyte: 0.1 M Na<sub>2</sub>SO<sub>4</sub>.

highly favorable energetically. The increase of the driving force accelerates the electron-transfer rate, and accordingly increases the photocurrent.<sup>42–45</sup>

In order to get insight into the mechanism of the photocurrent generation, the photoelectrochemical experiments were carried out in both deoxygenated and air-equilibrated supporting electrolyte solutions. As shown in Figure S13 (Supporting Information), the dissolved oxygen in the supporting electrolyte strongly influenced the photocurrent generation. When the supporting electrolyte was deoxygenated with bubbling N<sub>2</sub> for 30 min, the photocurrent decreased by 75% (from 40 to 10 nA), 69% (from 77 to 24 nA), and 54% (from 95 to 44 nA) as the applied potentials were set at -0.1, -0.2, and -0.3 V, respectively. So we can conclude that the

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dissolved oxygen played an important role in the process of photocurrent generation. Figure S14 (Supporting Information) shows the possible mechanism of the photocurrent generation. For highly *n*-doped semiconductors such as ITO, there are no unique values for the energies of the conduction band ( $E_C$ ) and valence band ( $E_V$ ) edges. However, from the electron affinity it is possible to estimate the value of  $E_C$  as approximately -4.5 eV.<sup>42,43</sup> When Re(CO)<sub>3</sub>(BIZ)(Py) in its ground state was excited by white-light irradiation (730 nm >  $\lambda$  > 325 nm), the excited-state Re(CO)<sub>3</sub>(BIZ)(Py)\* was formed, which was then oxidized by donating an electron to the electron acceptor dioxygen in the supporting electrolyte solution. The resulting oxidized Re(CO)<sub>3</sub>(BIZ)(Py)<sup>+</sup> was finally reduced by accepting an electron from the conduction band of ITO, completing the circuit.

In conclusion, a new N $\cap$ OH ligand-based monomeric Re(I) complex, Re(CO)<sub>3</sub>(BIZ)(Py), has been synthesized and structurally and spectroscopically characterized, which belongs to a rarely reported Re(CO)<sub>3</sub>(N $\cap$ O<sup>-</sup>)(X) family of complexes. The dimeric Re<sub>2</sub>(CO)<sub>6</sub>(BIZ)<sub>2</sub> in neat pyridine was found to convert into Re(CO)<sub>3</sub>(BIZ)(Py) at an intermediate rate constant of (3.9 ± 0.1) × 10<sup>-3</sup> M<sup>-1</sup> min<sup>-1</sup>. Re(CO)<sub>3</sub>(BIZ)(Py) in dichloromethane is weakly photoluminescent, with a quantum yield of ~0.2%. The modified electrode of Re(CO)<sub>3</sub>(BIZ)(Py) on ITO exhibited a large cathodic photocurrent up to 0.55  $\mu$ A/cm<sup>2</sup> under white-light irradiation of 100 mW/cm<sup>2</sup> at -0.3 V bias potential. This study would provide fundamental experimental data for potential applications of Re(CO)<sub>3</sub>(BIZ)(Py) in photoelectric conversion devices.

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**Supporting Information Available:** Experimental details and CIF files giving crystallographic data of Re(CO)<sub>3</sub>(BIZ)(Py). This material is available free of charge via the Internet at http://pubs.acs.org.

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