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Three Olefin Copper(I) Dimeric Complexes with 2-, 3-, and 4-Pyridylacrylic Acid and Their Electrochemical Properties

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UV irradiation of 2-, 3-, or 4-pyridylacrylic acid (2-, 3-, and 4-HPYA) with $Cu^{I}Cl$ at 230 nm in 4 N HCl for 1 week and subsequent hydrothermal reactions yielded three novel highly stable 3-D copper(I)–olefin dimers, $[(2\text{-}H_2PYA)_2Cu^{+}{}_2Cl_4]_n$ (**1**), $[(3\text{-}H_2PYA)_2Cu^{+}{}_2Cl_4]_n$ (**2**), and $[(4\text{-}H_2PYA)_2Cu^{+}{}_2Cl_4(I)]_n$ (**3**), respectively, in which H-bonds play a key role in the stabilization of supramolecular Cu(I)–olefin system and thus the formation of the 3-D networks. The electrochemical properties of **1**–**3** are also reported.

Introduction

Copper(I)−olefin complexes are used extensively in light-olefin/paraffin separation and enantio separation as the coordination of Cu(I) to η^2-olefin is labile. These complexes also take part in a variety of stress responses and developmental processes, as shown in the smallest plant hormone.[1,2] Recently, supramolecular motifs based on olefin−Cu(I) are a topic of intense interest,[3] particularly for their luminescent properties based on quenching of the guest−host interaction.[3d] It is worthy noting that, in the formation of many remarkably stable olefin−Cu(I) coordination polymers, bridging spacers by carboxylate and pyridyl groups often play a key role in stabilizing the supramolecular systems.[3] Stable discrete molecular Cu(I) complexes of bidentate olefin−carboxylate or pyridyl ligands such as 2-, 3-, and 4-pyridylacrylic acid with uncoordinated carboxylate or pyridyl groups are virtually unknown. It is difficult to avoid the binding of these carboxylate or pyridyl groups to Cu(I) ion to give polymeric structures.

Halides are known good bridging spacers in Cu(I)−olefin systems to give stable Cu(I)−olefin polymer with a prismane Cu_6X_6 cluster as connection corner unit.[4] We found that the UV irradiation at ca. 230 nm of a mixture of CuCl, 2-, 3-, and 4-pyridylacrylic acids (2-, 3-, and 4-HPYA), and HCl, followed by hydrothermal reactions, afforded three stable dimeric Cu−olefin complexes, $[Cu^{+}{}_2Cl_4(2\text{-}HPYCH{=}CHCOOH)_2]_n$, {or $[(2\text{-}H_2PYA)_2Cu^{+}{}_2Cl_4]_n$ (**1**)}, $[Cu^{+}{}_2Cl_4(3\text{-}HPYCH{=}CHCOOH)_2]_n$ {or $(3\text{-}H_2PYA)_2Cu^{+}{}_2Cl_4\}_n$ (**2**)}, and $[Cu^{+}{}_2Cl_4(4\text{-}HPYCH{=}CHCOOH)_2]_n$ {or $(4\text{-}H_2PYA)_2Cu^{+}{}_2Cl_4]_n$ (**3**)}. In these complexes, the pyridyl group is protonated to lose its coordination ability, and the carboxylate group is not bonded to Cu(I) either (Scheme 1). H-bonds among carboxyl groups as well as between the *H*−N atoms of the pyridyl ring and terminal Cl^- ligands gave 3-D networks of these stable Cu(I)−olefin complexes **1**−**3**. Herein we report

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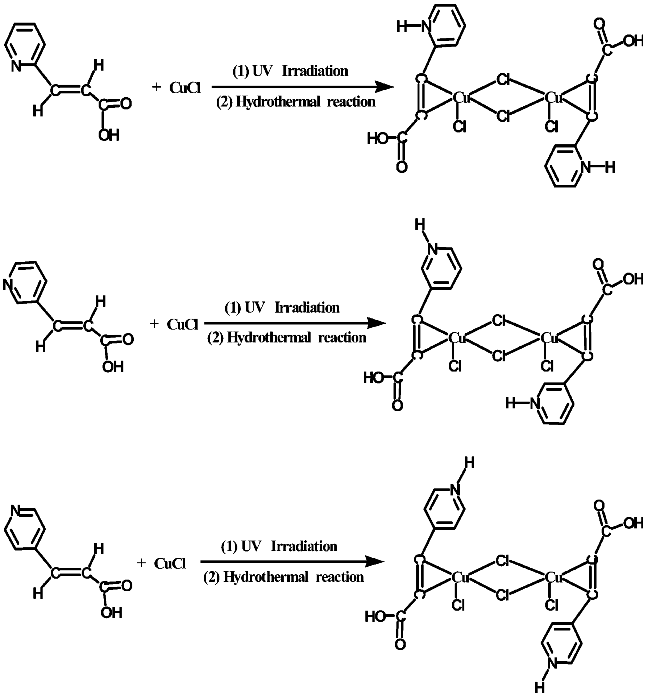
Scheme 1



the synthesis, solid-state structures, and electrochemical properties of **1**−**3**.

Results and Discussion

Compounds **1**−**3** were prepared respectively by hydrothermal reactions of Cu^ICl with 2-, 3-, and 4-HPYA in the presence of 1 N HCl after the mixtures were irradiated by UV at 230 nm for 1 week. The olefinic $\pi-\pi$ double bond may be activated under UV irradiation so that the reaction of olefin with Cu(I) easily took place because without UV irradiation; the same reaction under hydrothermal reaction conditions was not observed. Probably the hydrothermal reactions can also lead to good crystallization. In comparison to the IR spectra of free ligands, **1**−**3** show a peak at 1720−1690 cm^{-1}, indicating the carboxylates of 2-, 3-, and 4-HPYA in **1**−**3** are uncoordinated −COOH groups. **1**−**3** were found highly thermally stable, as the TGA of the polycrystalline **1**−**3** showed no weight loss before ca. 232, 183, and 168 °C, respectively. EPR spectra of single-crystal samples of **1**−**3** are silent, indicating that the oxidation state of the Cu atoms in **1**−**3** is +1.

The X-ray crystal analysis of compound **1** (Figure 1a) revealed that the Cu(I) ion in **1** is coordinated in a distorted tetrahedral geometry defined by two bridging μ_2-Cl^- ligands, one terminal Cl^- ligand, and the C=C moiety in 2-H_2PYA. Interestingly, the pyridyl group is protonated to lose its coordinating ability, and the carboxylate groups are uncoordinated as well. The carboxylate groups are H-bonded (O−H···O, 2.650 Å) with other $(2\text{-}H_2PYA)_2Cu_2Cl_4$ units. Strong H-bonds between protonated N atom and terminal Cl^- ligands (N−H···Cl, 3.232 Å) were also observed (Figure 1b). These strong H-bond interactions gave a 3-D network in **1** (Figure S1; see Supporting Information).

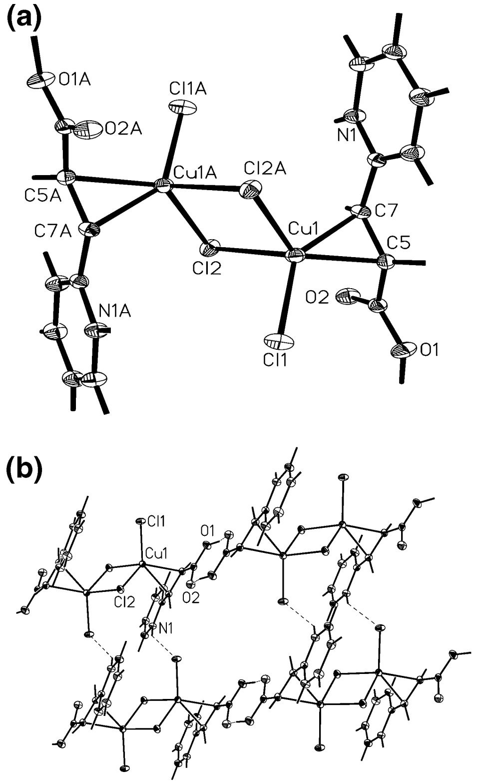


Figure 1. (a) Dimeric molecular structural representation of **1** (30% ellipsoid probability). Typical bond distances (Å) and angles (deg): Cu(1)−Cl(1) 2.2443(6), Cu(1)−Cl(2) 2.3205(6), Cu(1)−Cl(2A) 2.4870(6), Cu(1)−C(5) 2.066(2), Cu(1)−C(7) 2.092(2), C(5)−C(7) 1.375(3); C(5)−Cu(1)−C(7) 38.62(8), C(5)−Cu(1)−Cl(1) 103.62(6), C(7)−Cu(1)−Cl(2A) 105.47(6), Cl(1)−Cu(1)−Cl(2) 104.23(2), Cl(1)−Cu(1)−Cl(2A) 104.58(2), Cl(2)−Cu(1)−Cl(2A) 97.02(2), Cu(1)−Cl(2)−Cu(1A) 82.98(2). (b) 3-D network representation of **1** through H-bonds in which a carboxylic acid dimer was yielded via H-bonds.

The structure of **2** (Figure 2a) is similar to that of **1** with different H-bonds. H-bonds were found between the carboxylate group and terminal Cl^- ligand (O−H···Cl, 3.107 Å) as well as between the protonated N atom and bridging Cl^- ligand (N−H···Cl, 3.361 Å), as shown in Figure 2b, to give a 3-D network in **2** (Figure S2; see Supporting Information).

Similar to the structures of **1** and **2**, the local geometry of the Cu atom in **3** can be best described as a distorted tetrahedron with two μ_2 bridging Cl^- ligands, one terminal Cl^- ligand, and one olefin moiety. The H-bonds in **3** are similar to those in **1**. Strong H-bonds (O−H···O, 2.639 Å) between carboxylate groups (Figure 3 b) as well as between the protonated N atom and terminal Cl^- ligand (N−H···Cl, 3.405 Å) give a 3-D network in **3** (Figure S3; see Supporting Information).

The coordination mode of the carboxylate group in **1**−**3** is quite different from those of the Cu(I)−olefin coordination polymers found in $[(3\text{-PYA})Cu]_n$ (**4**), $\{[(2\text{-PYA})Cu]\cdot H_2O\}_n$ (**5**), and $[Cu_2(O_2CCH{=}CHCO_2)]_n$ (**6**)[3f] in which the carboxylate groups of **4** and **5**, in a *syn*−*syn* bidentate bridging mode, link two Cu atoms to form a chaired-type eight-membered ring while the carboxylate groups of fumaric acid act as tridentate ligands to link three Cu(I) atoms. The coordination mode of the carboxylate group in **1**−**3** is however similar to those found in {[(2,2′-bpy)(4-HPYA)-

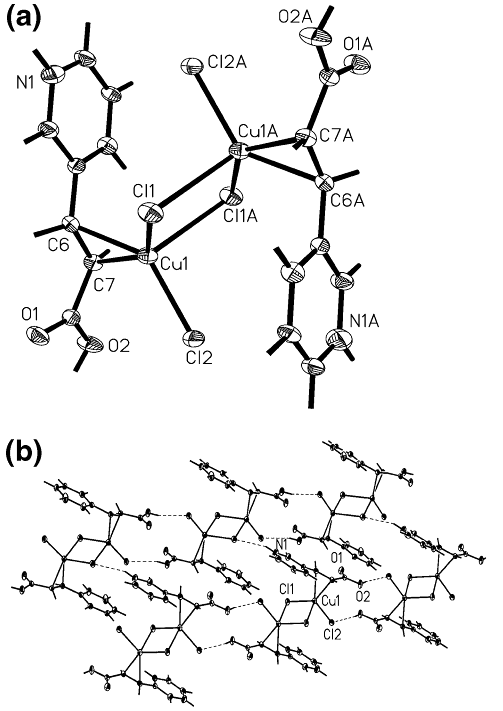


Figure 2. (a) Dimeric molecular structural representation of **2** (30% ellipsoid probability). Typical bond distances (Å) and angles (deg): Cu(1)−C(6) 2.084(3), Cu(1)−C(7) 2.063(3), C(6)−C(7) 1.372(4), Cu(1)−Cl(1) 2.2720(9), Cu(1)−Cl(2) 2.2635(10), Cu(1)−Cl(1A) 2.6368(10); C(6)−Cu(1)−C(7) 38.63(12), C(6)−Cu(1)−Cl(1A) 106.98(9), C(6)−Cu(1)−Cl(2) 137.45(9), C(7)−Cu(1)−Cl(1) 139.12(10), C(7)−Cu(1)−Cl(2) 103.43(10), Cl(1)−Cu(1)−Cl(1A) 93.12(3), Cl(1)−Cu(1)−Cl(2) 110.31(4), Cu(1)−Cl(1A)−Cu(1A) 86.88(3). (b) 3-D network representation of **1** through H-bonds in which a carboxylic acid dimer was created via H-bonds.

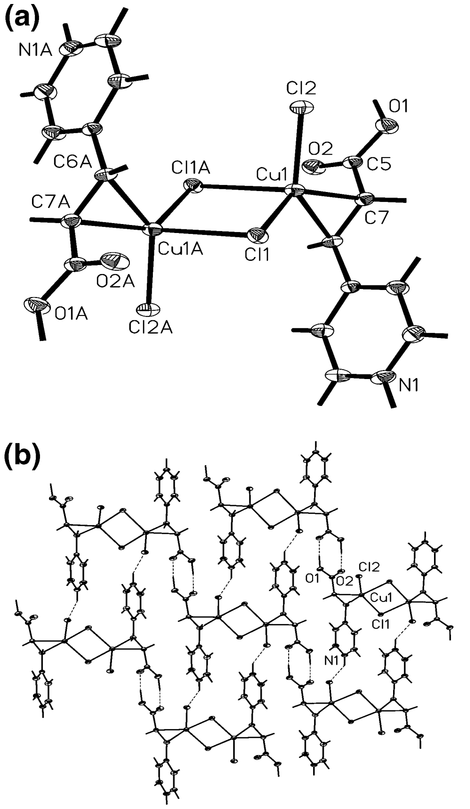


Figure 3. (a) Dimer molecular structural representation of **3** (30% ellipsoid probability). Typical bond distances (Å) and angles (deg): Cu(1)−C(6) 2.090(3), Cu(1)−C(7) 2.056(3), C(6)−C(7) 1.374(3), Cu(1)−Cl(1) 2.3016(7), Cu(1)−Cl(2) 2.22357(7), Cu(1)−Cl(1A) 2.5721(8); C(6)−Cu(1)−C(7) 38.70(10), C(6)−Cu(1)−Cl(1) 106.97(7), C(6)−Cu(1)−Cl(2) 141.45(7), C(7)−Cu(1)−Cl(1) 134.70(7), C(7)−Cu(1)−Cl(2) 103.06(7), Cl(1)−Cu(1)−Cl(1A) 95.99(3), Cl(1)−Cu(1)−Cl(2) 107.35(3), Cu(1)−Cl(1A)−Cu(1A) 84.01(2). (b) 3-D network representation of **3** through H-bonds in which a carboxylic acid dimer was created via H-bonds.

Cu](BF$_4$)}$_n$ (**7**),[3a] {[(1,10-phen)(4-HPYA)Cu](BF$_4$)}$_n$ (**8**),[3b] and {[(2,2′-bpy)(3-HPYA)Cu](BF$_4$)}$_n$ (**9**),[3b] in which the carboxylate groups are not coordinated to Cu. One major difference between the structures of **1**−**3** and **4**, **5**, and **7**−**9** is that the pyridyl groups in **1**−**3** are all protonated and are not coordinated to Cu(I), while these pyridyl groups in **4**, **5**, and **7**−**9** coordinated to Cu(I), resulting in the formation 1-D or 2-D coordination polymers.[3] It is noteworthy that the stable Cu(I)−olefin coordination polymers **1**−**9** form similar 3-D networks through H-bonds except that there are weak stabilizing π−π interactions of adjacent two pyridyl rings in **4** and **5**.[3b]

The C−C bond distances (1.372−1.375 Å) of the coordinated olefin moiety in **1**−**3** are slightly longer than those found in [Cu(2,2-bipy)(C$_2$H$_4$)]·ClO$_4$ [1.360(13)−1.346(18) Å],[5] [Cu(phen)(C$_2$H$_4$)]·ClO$_4$ [1.361(22) Å],[5] [Cu$_2$(HB(3,5-Me$_2$PZ)$_3$(C$_2$H$_4$))Cl] [1.347(5) Å],[6,7] [Cu(C$_2$H$_4$)(dipyridylamine)] [1.359(7) Å],[6,7] **6** [1.371(14) Å],[3f] [Bu$^t_2$P(NSiMe$_3$)$_2$-κ^2N]Cu-(η^2-C$_2$H$_4$) [1.362(6) Å],[8] [Cu(HB(3,5-Me$_2$PZ)$_3$)(C$_2$H$_4$)] [1.329(9) Å],[6] [Cu$_2$(COT)(hfacac)$_2$] [1.31(1)−1.33(1) Å],[9] **7** [1.361(6) Å],[3b] **8** [1.359(12) Å],[3b] and [Cu((*S*,*S*)-L)(1-buten-3-ol)][L = (1*S*,2*S*)-*N*,*N*′-bis(mesitymethyl)-1,2-diphenyl-1,2-ethanediamine, 1.36(1) Å][6] but are comparable to that in **9** [1.375(5) Å][3b] and **4** [1.367(7) Å].[3b] The lengthening of the C−C double bond may be typical of ethylene ligands that are η^2-bonded to low-valent electron-rich transition metals.[10] Moreover, the Cu−Cl$_{\text{terminal}}$ and Cu−Cl$_\mu$ (2.272−2.572 and 2.236−2.320 Å) bond lengths in **1**−**3** are normal and lie within the distances expected for Cu(I) complexes. The Cu−C bond distances (2.059−2.092 Å) in **1**−**3** are comparable to those found in other reported Cu(I) organometallic compounds.

As seen from Figure 4, the cyclic voltammograms of CuCl, [(2-H$_2$PYA)$_2$Cu$^I_2$Cl$_4$(I)]$_n$ (**1**), [(3-H$_2$PYA)$_2$Cu$^I_2$Cl$_4$]$_n$ (**2**), and [(4-H$_2$PYA)$_2$Cu$^I_2$Cl$_4$]$_n$ (**3**) complexes displayed one oxidation peak and a similar cathodic wave in the sweep range of +300 to −1100 mV. Their anodic peak potentials were −308, −300, −290, and −278 mV at 100 mV/s, respectively. No peak was observable in the solution of ligand, suggesting

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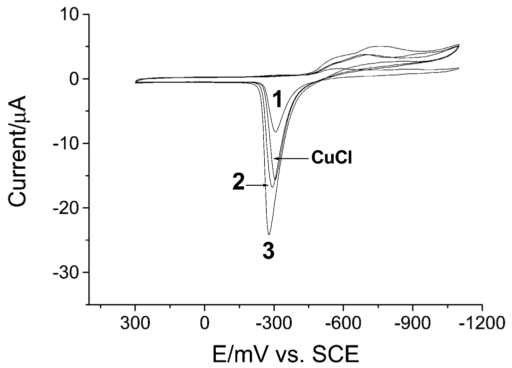

Figure 4. Cyclic voltammograms of 0.1 M Bu_4NClO_4 acetonitrile solutions containing 1.0 mM CuCl, $[(2\text{-}H_2PYA)_2Cu_2Cl_4]_n$ (**1**), $[(3\text{-}H_2PYA)_2Cu_2Cl_4]_n$ (**2**), and $[(4\text{-}H_2PYA)_2Cu_2Cl_4]_n$ (**3**) at 100 mV/s at a platinum disk working electrode.

that the anodic peaks were attributed to the oxidation of metal centers in complexes. The single oxidation peak indicated that two metal centers in complexes were in the same local coordination geometry. The cathodic peaks came from the reduction of Cu(I) centers to Cu. There are two metal centers in one complex molecule of **1**−**3**; the peak current of CuCl was larger than those of **1**−**3** at the same Cu mole number. More positive anodic peak potentials and lower peak currents of **1**−**3** than those of CuCl are a result of the Cu(I) centers by the H_2PYA^+ ligands. The decrease in anodic peak current was due to the smaller diffusion coefficient of these complexes. The resulting difference between the peak potentials of the three complexes may be due to different steady constants which is similar to that found in $[Cu_4Br_4(TTT)_2]_n$ and $[Cu_6Br_6(TTT)_2]_n$ [TTT = triallyl-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trone].[4]

Experimental Section

Preparation of 1. CuCl (1 mmol) and 2-HPYA (1 mmol) were placed in a thick Pyrex tube (ca. 20 cm in length). After addition of 0.3 mL of 4 N HCl, the tube was frozen with liquid N_2, evacuated under vacuum, and sealed with a torch. The tube was irradiated at 230 nm for 1 week at room temperature. The solution turns red, and the tube was then placed into oven at 105 °C for 2 days to give red-brown block crystals of **1** (0.157 g, 55% yield) based on 2-HPYA. Anal. Found: C, 45.24; H, 2.76; N, 6.45. Calcd: C, 45.39; H, 2.86; N, 6.62. IR (KBr, cm^{-1}): 3449 (w), 3080 (w), 3020 (w), 2685 (w), 1698 (vs), 1633 (m), 1594 (w), 1473 (m), 1427 (m), 1310 (s), 1284 (s), 1257 (w), 1226 (w), 1207 (w), 1166 (w), 1100 (w), 1058 (w), 978 (m), 943 (w), 900 (w), 781 (m), 747 (w), 702 (w), 613 (w), 549 (w), 487 (w).

Preparation of 2. The procedures were similar to those of **1** except that 3-HPYA was used instead of 2-HPYA. The tube was heated at 105 °C for 2 days to give red-yellow block crystals of **2** (0.185 g, 65% yield) based on 3-HPYA. Anal. Found: C, 41.83; H, 3.51; N, 6.10. Calcd: C, 42.03; H, 3.66; N, 6.15. IR (KBr, cm^{-1}): 3191 (m), 3150 (s), 3118 (s), 3087 (w), 3050 (w), 1716 (vs), 1649 (m), 1594 (m), 1536 (s), 1457 (m), 1386 (s), 1284 (m), 1249 (w), 1224 (m), 1189 (s), 1173 (m), 1104 (w), 1038 (w), 1025 (w), 998 (w), 956 (w), 877 (w), 850 (w), 795 (m), 696 (m), 667 (w), 588 (w), 525 (w), 488 (w).

Preparation of 3. The procedures are similar to those of **1** except that 4-HPYA was used instead of 2-HPYA. The tube was heated at 105 °C for 2 days to give red needles crystals of **3** (0.199 g, 70% yield) based on 4-HPYA. Anal. Found: C, 41.83; H, 3.51; N, 6.10. Calcd: C, 42.03; H, 3.66; N, 6.15. IR (KBr, cm^{-1}): 3068 (m), 1718 (w), 1677 (vs), 1627 (vs), 1585 (m), 1551 (w), 1495 (w), 1482 (m), 1407 (w), 1382 (w), 1318 (w), 1298 (m), 1261 (w), 1230 (w), 1206 (w), 1192 (w), 1176 (w), 1085 (w), 1059 (w), 1005 (w), 981 (w), 944 (w), 922 (w), 875 (w), 851 (w), 808 (m), 737 (w), 705 (w), 695 (w), 645 (w), 583 (w), 548 (w), 517 (w).

X-ray Crystallographic Determination of 1−3. Crystal data for 1: $C_8H_8Cl_2CuNO_2$, $M_r = 284.59$, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.1801(5)$ Å, $b = 8.6980(6)$ Å, $c = 8.8516(6)$ Å, $\alpha = 77.719(1)°$, $\beta = 74.348(1)°$, $\gamma = 70.963(1)°$, $V = 498.45(6)$ Å^3, $Z = 2$, $T = 293(2)$ K, $\rho_{cacl} = 1.896$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.710\,73$ Å), $\mu = 2.695$ mm^{-1}, $R_1 = 0.0405$, $wR_2 = 0.0588$ for 2563 observed reflections from 3485 independent reflections, GOF = 1.278.

Crystal data for 2: $C_8H_8Cl_2CuNO_2$, $M_r = 284.59$, monoclinic, space group $P2_1/n$, $a = 9.8845(9)$ Å, $b = 9.6189(9)$ Å, $c = 10.9299(10)$ Å, $\beta = 106.604(2)°$, $V = 995.86(16)$ Å^3, $Z = 4$, $T = 293(2)$ K, $\rho_{cacl} = 1.898$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.710\,73$ Å), $\mu = 2.698$ mm^{-1}, $R_1 = 0.0334$, $wR_2 = 0.0812$ for 1468 observed reflections from 1758 independent reflections, GOF = 1.024.

Crystal data for 3: $C_8H_8Cl_2CuNO_2$, $M_r = 284.59$, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.2107(9)$ Å, $b = 8.5682(11)$ Å, $c = 8.7294(11)$ Å, $\alpha = 76.575(3)°$, $\beta = 79.859(3)°$, $\gamma = 71.527(2)°$, $V = 494.48(11)$ Å^3, $Z = 2$, $T = 293(2)$ K, $\rho_{cacl} = 1.911$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.710\,73$ Å), $\mu = 2.717$ mm^{-1}, $R_1 = 0.0375$, $wR_2 = 0.0676$ for 2159 observed reflections from 3476 independent reflections, GOF = 0.750.

Electrochemical Properties of 1−3. Electrochemical studies were performed with a BAS 100 B electrochemical analyzer (Bioanalytical Systems Inc.) using a standard three-electrode system comprising a saturated calomel electrode (SCE) as reference, a platinum wire as auxiliary electrode. and a platinum disk (1.0 mm diameter) as working electrode. The working electrodes were polished to a mirrorlike surface with 0.3 and 0.05 μm alumina slurry on microcloth pads (Buehler), rinsed with water and ethanol, and sonicated in twice-distilled water. After being dried in heated air, the electrodes were used for electrochemical experiments in the deaerated acetonitrile solutions by purging with pure nitrogen for 15 min.

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Supporting Information Available: Crystallographic CIF files (excluding structure factors) for **1**−**3** and an additional figure. This material is available free of charge via the Internet at http://pubs.acs.org.

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