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Two Luminescent 2D Layered Copper(I)−Olefin Coordination Polymers with High Thermal Stability

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*Summary: The solvothermal reactions of 3-pyridylacrylic acid (3-HPYA) and 2-pyridylacrylic acid (2-HPYA) with $Cu(CH_3CN)_4BF_4$ yield two novel highly stable copper(I)−olefin coordination polymers, [(3-PYA)Cu(I)]n (**1**) and {[(2-PYA)Cu(I)]·(H_2O)}n (**2**), respectively. Both polymers display 2D layered structures and yellow fluorescent emission in the solid state.*

Introduction

Copper-catalyzed addition of carbanions to α,β-unsaturated carbonyls and copper-catalyzed cyclopropanation of alkenes by α-carbonyl diazoalkanes involve copper(I)−olefin complexes as catalytically active species or resting state.[1] Copper(I)−ethylene complexes may also participate in a variety of stress responses and developmental processes, as in the smallest plant hormone, an ethylene group binds tightly to the copper receptor site ETR.[2] Recently, chiral recognition through the coordination of Cu(I)−olefin is also a topic of intense interest, particularly for its involvement in metal-promoted enantioselective synthesis.[3] It is thus important to further investigate the chemistry and biochemistry of copper(I)−olefin complexes. The pioneering work of Thompson and co-workers demonstrated the first stable copper(I)−olefin complexes in 1983.[4] Since then, there have been many Cu(I)−olefin complexes documented in the literatures, such as $[Cu(C_2H_4)(\text{dipyridylamine})]$, $[Cu_2(HB(3,5\text{-}Me_2PZ)_3(C_2H_4))Cl](HB(3,5\text{-}Me_2PZ)$ = hydrotris(3,5-dimethyl-1-pyrazolylborate),[4,5] $[Cu(2,2\text{-bipy})(C_2H_4)]\cdot ClO_4$, $[Cu(\text{phen})(C_2H_4)]\cdot ClO_4$,[6] $[Cu(O_2CCF_3)$(Z,E,E)-1,5,9-cyclododecatriene],[6c] $[Cu_2(COT)(hfacac)_2]$ (COT = 1,3,5,7-cyclooctatetraene, hfacac = hexafluoroacetylacetone),[7] and $[Bu^t{}_2P(NSiMe_3)_2\text{-}\kappa^2N]Cu(\eta^2\text{-}C_2H_4)$.[8] As expected, all these reported complexes are air-sensitive and molecular in nature. Recently, Schultz and co-workers prepared a unique, dense metal−organic layered framework containing η^2-copper(I)−olefinic bonds, a monofumarate dicopper(I) complex, by using crystal engineering strategies under hydrothermal reaction conditions.[9] They suggested that high air-stability of copper(I)−olefin layered framework (up to 300 °C) may be due to the high concentration of bonding and exclusion of water in the lattice. We have demonstrated three highly stable Cu(I)−olefin 1D coordination polymers, $\{[(2,2'\text{-bpy})(4\text{-HPYA})Cu(I)](BF_4)\}n$, $\{[(1,10\text{-phen})(4\text{-HPYA})Cu(I)](BF_4)\}n$, and $\{[(2,2'\text{-bpy})(3\text{-HPYA})Cu(I)](BF_4)\}n$ (4-HPYA = 4-pyridylacrylic acid, 3-HPYA = 3-pyridylacrylic acid), in which the highly stable copper(I)−olefin complexes may be the result of the high concentration of hydrogen bonding and $\pi-\pi$ stacking between two adjacent strands.[10] However, we were unsuccessful then to obtain the neutral Cu(I)−olefin coordination polymers {[(2,2′-bpy)(4-PYA)Cu(I)]}*n*, [(1,10-phen)(4-PYA)Cu(I)], and [(2,2′-bpy)(3-PYA)Cu(I)] or [(4-PYA)Cu(I)]*n* and [(3-PYA)Cu(I)]*n* even if the reaction occurred in weak basic solution. To our surprise, the reactions of 3-HPYA and 2-HPYA with $Cu(CH_3CN)_4BF_4$ afford two 2D neutral Cu(I)−olefin coordination polymers [Cu(3-PYA)]*n* (**1**) and {[(2-PYA)Cu(I)]·(H_2O)}*n* (**2**), respectively (Scheme 1), in the presence of PPh_3. Here we report their synthesis, solid state structure, thermal stability, and fluorescent property of **1** and **2**. To our knowledge, both **1** and **2** represent the first example of 2D Cu(I)−olefin coordination polymers with yellow fluorescent emission.[9]

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(1) (a) Hallnemo, G.; Olsson, T.; Ullenius, C. *J. Organomet. Chem.* **1985**, *282*, 133. (b) Mori, S.; Nakamura, E. *Chem. Eur. J.* **1999**, *5*, 1534. (c) Diaz-Requejo, M. M.; Nicasio, M. C.; Perez, P. J. *Organometallics* **1998**, *17*, 3051. (d) Diaz-Requejo, M. M.; Belderrain, T. R.; Nicasio, M. C.; Prieto F.; Perez, P. J. *Organometallics* **1999**, *18*, 2601. (e) Striejewske, W. S.; Conry, R. R. *Chem. Commun.* **1998**, 555. (f) Shimazaki, Y.; Yokoyama, H.; Yamauki, O. *Angew. Chem., Int. Ed.* **1999**, *38*, 2401. (g) Diaz-Requejo, M. M.; Belderrain, T.; Perez, P. J. *Chem. Commun.* **2000**, 1853.

(2) (a) Schaller, G. E.; Bleecker, A. B. *Science* **1995**, *270*, 1809. (b) Rodriguez, F. I.; Esch, J. J.; Hall, A. E.; Binder, B. M.; Schaller, G. E.; Bleecker, A. B. *Science* **1999**, *283*, 996. (c) Ecker, J. R. *Science* **1995**, *268*, 667.

(3) Cavallo, L.; Cucciolito, M. E.; Martino, A. D.; Giordano, F.; Orabona I.; Vitagliano, A. *Chem. Eur. J.* **2000**, *6*, 1127, and references therein.

(4) (a) Thompson, J. S.; Harlow, R. L.; Whitney, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3522. (b) Thompson, J. S.; Whitney, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 5488.

(5) (a) Thompson, J. S.; Whitney, J. F. *Inorg. Chem.* **1984**, *23*, 2813. (b) Thompson, J. S.; Harlow , R. L.; Swiatek, M. *Inorg. Chem.* 1**985**, *24*, 110.

(6) (a) Masuda, H.; Yamamoto, N.; Taga, T.; Machida, K.; Kitagawa, S.; Munakata, M. *J. Organomet. Chem.* **1987**, *322*, 121. (b) Munakata, M.; Kitagawa, S.; Kosomo, S.; Asahara, A. N. *Inorg. Chem.* **1986**, *25*, 2622. (c) Reger, D. L.; Dukes, M. D. *J. Organomet. Chem.* **1976**, *113*, 173.

(7) Doyle, G.; Eriksen, K. A.; Engen, D. Van *Organometallics* **1985**, *4*, 830.

(8) Straub, B. F.; Eisentrer, F.; Hofmann, P. *Chem. Commun.* **1999**, 2507.

(9) Young, D. M.; Geiser, U.; Schultz, A. J.; Wang, H. H. *J. Am. Chem. Soc.* **1998**, *120*, 1331.

(10) (a) Zhang, J.; Xiong, R.-G.; Zuo, J.-L.; You, X.-Z. *Chem. Commun.* **2000**, 1495. (b) Zhang, J.; Xiong, R.-G.; Zuo, J.-L.; Che C.-M.; You, X.-Z. *J. Chem. Soc., Dalton. Trans.* **2000**, 2898.

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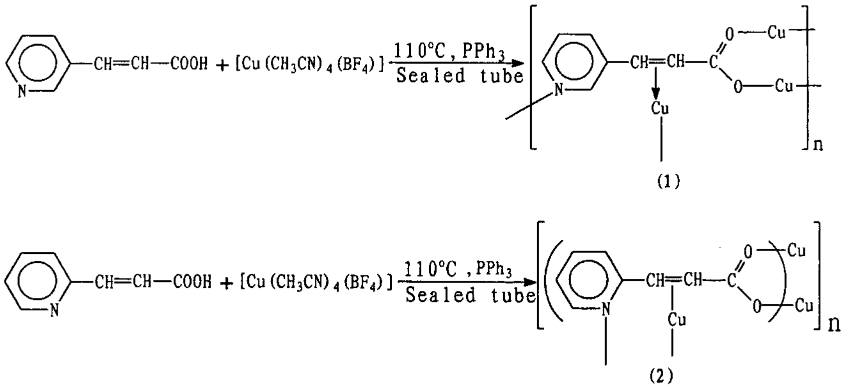
Scheme 1



Results and Discussion

Compounds **1** and **2** were prepared under solvothermal reaction conditions by reactions of Cu(MeCN)$_4$(BF$_4$) with 3-HPYA and 2-HPYA in the presence of PPh$_3$, respectively. In comparison to the IR spectra of {[(2,2′-bpy)(4-HPYA)Cu(I)](BF$_4$)}*n* and {[(2,2′-bpy)(3-HPYA)-Cu(I)](BF$_4$)}*n*,[10] those of complexes **1** and **2** show no peak at 1072 cm^{-1}, indicating there no longer exists BF$_4^-$ anions. Furthermore there is a strong peak at 1600 cm^{-1} for **1** and at 1616 cm^{-1} for **2** in their IR spectra, and neither showed a peak at ca. 1700 cm^{-1}. In comparison to those of free 3-HPYA and 2-HPYA, the IR of **1** and **2** suggest 3-HPYA and 2-HPYA were deprotonated. We have so far not been able to obtain single crystals of [(4-PYA)Cu(I)]*n* (4-pyridylacrylic acid = 4-PYA) suitable for X-ray analysis by using a procedure similar to those to yield **1** and **2**, probably because 4-PYA is not flexible enough to coordinate to copper atoms. **1** and **2** possess high thermal stability, as shown in their thermogravimetric analysis. The TGA of the polycrystalline **1** showed no weight loss between ca. 50 and 265 °C, while that of polycrystalline **2** indicated a weight loss (7.60%) between ca. 50 and 245 °C, perhaps as a result of the removal of one water per formula unit (7.91%). The framework collapses beyond 265 °C for **1** and 245 °C for **2**, respectively. EPR spectra of single-crystal samples of both **1** and **2** are silent, indicating that the status of Cu atoms in **1** and **2** is Cu(I).

The X-ray crystal analysis of complexes **1** and **2** (Figure 1) revealed that Cu(I) ions in **1** and **2** are coordinated in a distorted tetrahedral geometry, which is defined by two oxygen atoms and one nitrogen atom (from three different 3-PYA ligands for **1** and from three different 2-PYA ligands for **2**) and the C−C moiety of the olefin (of 3-PYA for **1** and 2-PYA for **2**). Thus, both ligands 3-PYA and 2-PYA act as an anion tetradentate spacer to link four Cu(I) ions by using two carboxylate oxygen atoms, one N atom of the pyridyl ring, and the olefin moiety to give rise to a 2D coordination polymer, as depicted in Figure 2. Each carboxylate group in **1** adopts a syn−syn bidentate bridging mode to link two Cu atoms to form a chair-type eight-membered ring (Cu1−O2−C8−O1−Cu1A−O2A−C8A−O1A), while each eight-membered ring in **2** (Cu2−O2−C1−C4−Cu3−O5−C5−C6, Cu2−O3−C2−O4−Cu1−O1−C1−O2, and Cu1−C10−C12−N1−Cu4−C11−C8−N2) includes two Cu(I) atoms; thus the carboxylate of 2-PYA acts as a bidentate bridging ligand to link two Cu(I) atoms. The coordination mode of carboxylate groups in **1** and **2** is quite different from that in [Cu$_2$(O$_2$CCH=CHCO$_2$)], in which the carboxylate of fumaric acid acts as a tridentate ligand to link three Cu(I) atoms, resulting in the formation of a dense compound with a large density of 3.24 g cm^{-3}.[9] Similar to those in {[(2,2′-bpy)(4-HPYA)-Cu(I)](BF$_4$)}*n*, {[(1,10-phen)(4-HPYA)Cu(I)](BF$_4$)}*n*, and {[(2,2′-bpy)(3-HPYA)Cu(I)](BF$_4$)}*n*,[10] there are weak stabilizing $\pi-\pi$ interactions (ca. 4.07 Å for **1** and 3.427 Å for **2**) of adjacent two pyridyl rings, probably suggesting that $\pi-\pi$ stacking of neighboring strands plays an important role in stabilizing the Cu(I)−olefin complexes. The crystal packing (Figure 3a) in **1** indicates that the

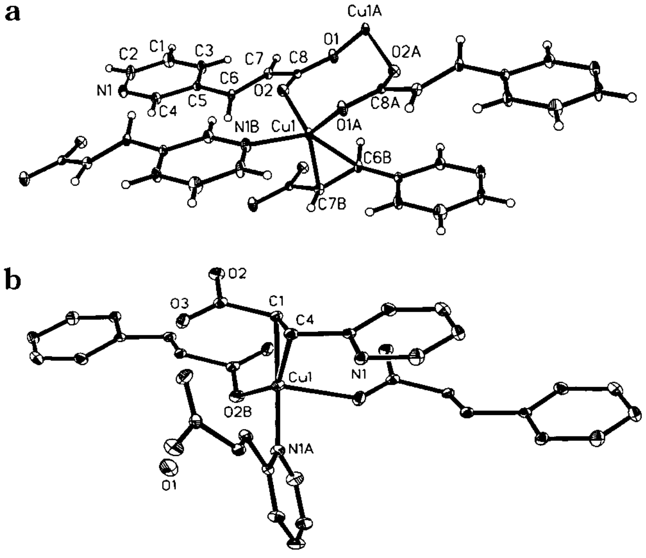


Figure 1. (a) ORTEP diagram of an asymmetric unit of **1** (30% ellipsoid probability). Selected bond lengths [Å] and angles [deg]: Cu(1)−N(1C) 2.015(4), Cu(1)−O(1A) 1.989(3), Cu(1)−O(2) 2.139(3), Cu(1)−C(6B) 2.074(5), Cu(1)−C(7B) 2.041(5), C(6)−C(7) 1.375(5); O(1A)−Cu(1)−N(1) 99.85(16), O(1A)−Cu(1)−C(7B), 132.26(18), N(1C)−Cu(1)−C(7B) 102.94(19), O(1A)−Cu(1)−O(2) 119.12(14), N(1C)−Cu(1)−O(2) 92.52(16), C(7B)−Cu(1)−O(2) 101.22(16), C(6B)−Cu(1)−O(2) 102.23(17), C(6B)−Cu(1)−C(7B) 38.79(19). (b) ORTEP diagram of an asymmetric unit of **2** (30% ellipsoid probability). Selected bond lengths [Å] and angles [deg]: Cu(1)−N(1A) 2.022(3), Cu(1)−O(2B) 2.014(3), Cu(1)−O(3C) 2.224(3), Cu(1)−C(1) 2.040(4), Cu(1)−C(4) 2.062(4), C(1)−C(4) 1.395(5); O(2B)−Cu(1)−O(3C) 103.91(14), N(1A)−Cu(1)−O(3C) 103.91(14), C(1)−Cu(1)−C(4) 39.76(14), C(1)−Cu(1)−O(2B) 103.06(14), C(4)−Cu(1)−O(2B) 139.99(14), N(1A)−Cu(1)−C(1) 155.46(14), N(1A)−Cu(1)−C(4) 116.56(13), C(1)−Cu(1)−O(3C) 85.65(12), C(4)−Cu(1)−O(3C) 100.06(12).

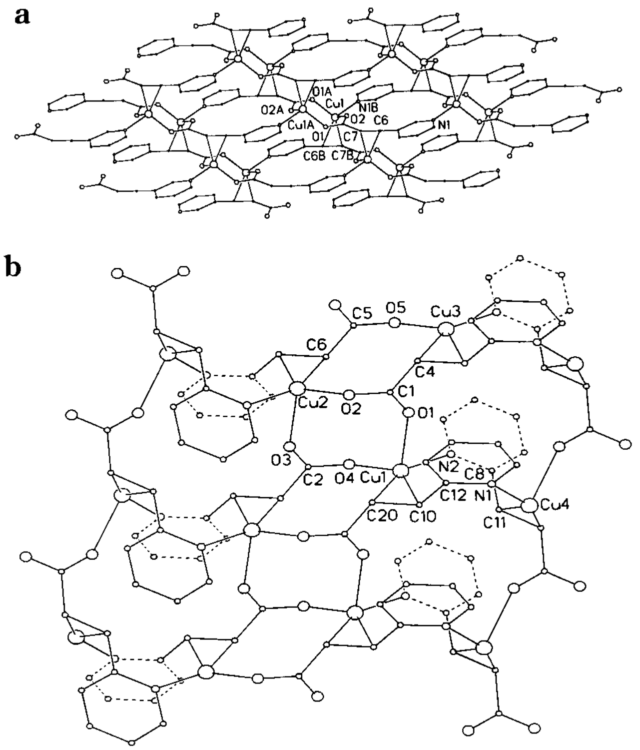


Figure 2. (a) Extended 2D layered representation of **1** showing $\pi-\pi$ stacking between adjacent strands. (b) An extended 2D layered representation of **2** showing $\pi-\pi$ stacking between adjacent strands (dotted pyridyl rings are below the plane).

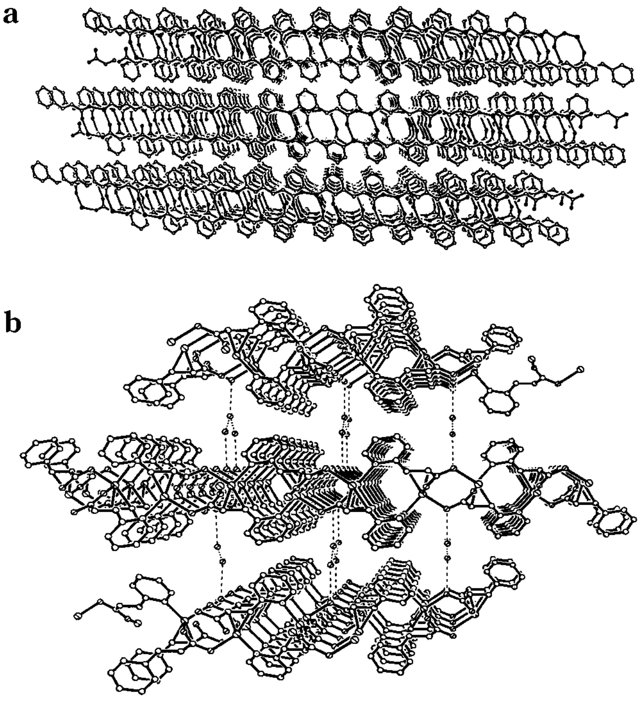


Figure 3. (a) Crystal packing view showing the support of pyridyl rings to the layers of **1**. (b) Crystal packing perspective view of **2** showing how the water molecule is intercalated between two adjacent layers.

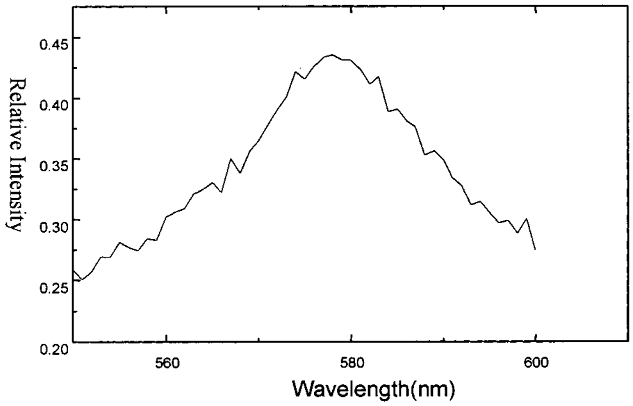


Figure 4. Fluorescent emission spectrum of **1** and **2** in the solid state at room temperature.

pyridyl rings act as pillars to support the layers, while in **2** the crystal packing (Figure 3b) indicates that water molecules are intercalated between two adjacent layers, and they are interlinked by a strong hydrogen bonding (2.913 Å) between water and the O atom of the carboxylate group.

The C−C bond distance (1.367(7) Å for **1** and 1.395(5) Å for **2**) of the coordinated olefin is slightly longer than those found in $[Cu(2,2\text{-bipy})(C_2H_4)]\cdot ClO_4$ (1.360(13)−1.346(18) Å),[6] $[Cu(phen)(C_2H_4)]\cdot ClO_4$ (1.361(22) Å),[6] $[Cu_2(HB(3,5\text{-}Me_2PZ)_3(C_2H_4))Cl]$ (1.347(5) Å), $[Cu(C_2H_4)(dipyridylamine)]$ (1.359(7) Å),[4,5] $[Cu_2(O_2CCH{=}CHCO_2)]$ (1.371(14) Å),[9] $[Bu^t_2P(NSiMe_3)_2\text{-}\kappa^2N]Cu(\eta^2\text{-}C_2H_4)$ (1.362(6) Å),[8] $[Cu(HB(3,5\text{-}Me_2PZ)_3)(C_2H_4)]$ (1.329(9) Å),[4] $[Cu_2(COT)(hfacac)_2]$ (1.31(1)−1.33(1) Å),[7] $\{[(2,2'\text{-bpy})(4\text{-HPYA})Cu(I)](BF_4)\}n$ (1.361(6) Å),[10] $\{[(1,10\text{-phen})(4\text{-HPYA})Cu(I)](BF_4)\}n$ (1.359(12) Å),[10] and [Cu((S,S)-L)(1-buten-3-ol)] (L = (1*S*,2*S*)-*N*,*N*′-bis(mesitymethyl)-1,2-diphenyl-1,2-ethane-diamine, 1.36(1) Å),[3] but is comparable to that in $\{[(2,2'\text{-bpy})(3\text{-HPYA})Cu(I)](BF_4)\}n$ (1.375(5) Å).[10]

Finally, 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.[11] Moreover, the Cu−N (2.015(3) Å for **1** and 2.022(3) Å for **2**) and Cu−O (1.989(3)−2.139(3) Å for **1** and 2.014(3) Å for **2**) bond lengths in **1** and **2** are normal and lie within the distances expected for Cu(I) complexes. The Cu−C bond distances (2.041(4)−2.074(4) Å for **1** and 2.040(4)−2.062(4) Å for **2**) in **1** and **2** are comparable to those found in other reported copper(I) organometallic compounds.

The luminescent spectra of **1** and **2** in the solid state at room temperature are shown in Figure 4, with a maximum at ca. 580 nm ($\lambda_{ex} = 250$ nm) that is similar to those found in $Cu_4I_4(pyridine)_4$ ($\lambda_{emax} = 580$ nm) and $[Cu(3,4'\text{-bipyridine})(Br)]n$ ($\lambda_{emax} = 580$ nm).[12] The diffuse reflectance UV−vis spectra of **1** and **2** show a high-energy band at ca. 275 nm for **1** and 330 nm for **2** and a low-energy band at ca. 404 nm for **1** and 406 nm for **2**. The former may be assigned to the intraligand transition of the free ligand due to 3-HPYA and 2-HPYA as they show a band at similar wavelength (280 nm for 3-HPYA and 310 nm for 2-HPYA), while the low-energy

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(11) (a) Iael, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33. (b) Mingos, D. M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 3, pp 1−88.

(12) (a) Fun, H.-K.; Raj, S. S. S.; Xiong, R.-G.; Zuo, J.-L.; Yu, Z.; Zhu, X.-L.; You, X.-Z. *J. Chem. Soc., Dalton Trans.* **1999**, 1711. (b) Kyle, K. R.; Ryu, C. K.; DiBenedetto, J. A.; Ford, P. C. *J. Am. Chem. Soc.* **1991**, *113*, 2954. (c) Henary, M.; Wootton, J. L.; Khan, S. I.; Zink, J. I. *Inorg. Chem.* **1997**, *36*, 796. (d) Miller, M. T.; Gantzel, P. K.; Karpishin, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 4292.

band should be assigned to a metal-to-ligand charge transfer (MLCT).[13] However, the metal center d to s orbital transition is not ruled out.[12c] This suggests that the emission at 580 nm in **1** and **2** can be tentatively ascribed to MLCT since the fluorescent emission of free ligand in the solid state is observed at 375 nm for 3-HPYA and 382 nm for 2-HPYA, respectively. In addition, the short luminescent lifetime of **1** (ca. $\tau = 1.06$ ns) and **2** (ca. $\tau = 0.96$ ns) in the solid state suggests their emission should be fluorescent emission.[14]

In conclusion, 2D layered copper(I)–olefin coordination polymers were preapred. In **1** and **2**, the geometric influence and flexibility of 3-HPYA and 2-HPYA ligands is vital to the formation of these 2D neutral Cu(I)–olefin coordination polymers.

Experimental Section

Preparation of 1. $Cu(MeCN)_4BF_4$ (1 mmol), 3-HPYA (1 mmol), and PPh_3 (1 mmol) were placed in a thick Pyrex tube (ca. 20 cm in length). After addition of 0.1 mL of water and 2.5 mL of *n*-butanol, the tube was frozen with liquid N_2, evacuated under vaccum, and sealed with a torch. The tube was heated at 110 °C for 2 days to give pale yellow block crystals (pure phase) in 65% yield based on 3-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}): 3402(m), 1645(w), 1600(s), 1480(w), 1420(m), 1390(s), 1360(s), 1261(w), 1240(w),1190(w), 980(w), 810(m),740(w), 695(m), 383(br m), 223(m), and 118.5(w).

Preparation of 2. $Cu(MeCN)_4BF_4$ (1 mmol), 2-HPYA (1 mmol), and PPh_3 (1 mmol) were placed in a thick Pyrex tube (ca. 20 cm in length). After addition of 0.1 mL of water and 2.5 mL of *n*-butanol, the tube was frozen with liquid N_2, evacuated under vaccum, and sealed with a torch. The tube was heated at 110 °C for 2 days to give pale yellow block crystals (pure phase) in 75% yield based on 2-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}): 3375(m), 1616(s), 1560(m), 1510(w), 1461(m), 1431(w), 1348(s), 1291(w), 1240(w), 1160(w), 860(w), 780(m), 610(w),435(m), 391(m), 265(br m), 212(w), and 124(w). We are grateful to a referee for suggesting to us that the ^{31}P NMR regarding the remaining solutions of **1** and **2** is at ca. −3.0 ppm, probably suggesting the formation of $[HPR_3]^+$-$[BF_4]^-$.[15] In addition, **1** and **2** can also be prepared by using ammonia instead of PPh_3.

X-ray Crystallographic Determination of 1 and 2. Crystal data for **1**: $C_{16}H_{12}Cu_2N_2O_4$, $M_r = 423.36$, triclinic, space group $P1$ (No.2), $a = 5.4620(11)$ Å, $b = 6.9400(14)$ Å, $c = 10.435(2)$ Å, $\alpha = 95.35(2)°$, $\beta = 104.56(3)°$, $\gamma = 110.13(3)°$, $V = 352.35.1(12)$ Å^3, $Z = 1$, $T = 293(2)$ K, $\rho_{cacl} = 1.995$ g cm^{-3}. Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 3.043$ mm^{-1}, $R_1 = 0.0332$, $wR_2 = 0.1149$ for 1111 observed reflections from 1231 independent reflections, GOF = 1.388.

Crystal data for **2**: $C_{16}H_{16}Cu_2N_2O_6$, $M_r = 459.39$, orthorhombic, space group *Pbcn*, $a = 20.149(4)$ Å, $b = 5.1578(10)$ Å, $c = 15.397(3)$ Å, $V = 1600.1(5)$ Å^3, $Z = 4$, $T = 293(2)$ K, $\rho_{cacl} = 1.907$ g cm^{-3}. Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 2.697$ mm^{-1}, $R_1 = 0.0288$, $wR_2 = 0.1080$ for 1165 observed reflections from 1411 independent reflections, GOF = 0.568.

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Supporting Information Available: Crystallographic CIF (excluding structure factors) and tables of atomic coordinates, thermal parameters, and bond distances and angles for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] (a)Yam, V. W.-W.; Lo, K. K.-W. *Chem. Soc. Rev.* **1999**, *28*, 323, and references therein. (b) Cunningham, C. T.; Cunningham, K. L. H.; Michalec, J. F.; McMillin, D. R. *Inorg. Chem.* **1999**, *38*, 4388. (c) McMillin, D. R.; McNett, K. M. *Chem. Rev.* **1998**, *98*, 1201.

[14] (a) Ford, P. C.; Cariati, E.; Bourassa, J. *Chem. Rev.* **1999**, *99*, 3625, and references therein. (b)Harvey, P. D.; Drouin, M.; Zhang, T. *Inorg. Chem.* **1997**, *36*, 4998.

[15] Grim S. O.; Yankowsky, A. W. *J. Org. Chem.* **1977**, *42*, 1236.