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A highly stable copper(I)-olefin coordination polymer with strong red fluorescent emission

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Under solvothermal conditions, the reaction of 4-pyridylacrilic acid (4-hpya) and 2,2′-bipyridine (bpy) with $Cu(MeCN)_4BF_4$ gives rise to an unprecedented stable copper(I)-olefin coordination polymer $\{[(bpy)(4\text{-}hpya)Cu(I)](BF_4)\}_n$ 1 which displays strong red fluorescent emission in the solid state.

Since the pioneering work of Thompson *et al.*[1] demonstrated the first stable copper(I)–olefin complexes, in which a tridentate ligand, hydrotris(3,5-dimethylpyrazol-1-yl)borate [HB(3,5-$Me_2pz)_3$], was used to stabilize the complexes, many copper(I)–olefin complexes have been reported in which bidentate ligands such as 2,2′-bipyridine(bpy) and its derivatives, di-2-pyridylamine,[2] 2,2-bipyridine[3] and 1,10-phenanthroline,[3] were used. An excellent example was shown by Doyle *et al.*[4] in which a β-diketonate was introduced to chelate the copper(I)–olefin complex. Recently, a tridentate ligand, *N*-(3-indolylethyl)-*N*,*N*′-bis(6-methyl-2-pyridylmethyl)amine (Me_2iep) and a macrocyclic ligand, *N*-[2-(1-naphthyl)ethyl]-1-aza-4,8-dithiacyclodecane, have been used to stablize copper(I)-η^2-indole[5] and copper(I)–η^2-naphthyl[5] complexes. Moreover, Hoffmann and coworkers have successfully prepared a remarkable stable (up to 108 °C) copper(I)–ethylene complex in which iminophosphanamide derivatives were used as chelating stabilizers to fix the ethylene.[6] However, it should be noted that all the above-mentioned complexes are air-sensitive and molecular in nature. More recently, Schultz and co-workers have utilized crystal engineering strategies to synthesize a unique dense monofumarate dicopper(I) metal–organic layered framework containing η^2-copper(I)–olefinic bonds.[7] They suggested that the high air stability of the 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.

In this work we have combined the above-mentioned synthetic strategies and designed *trans*-4-pyridylacrilic acid (4-hpya) as a building block to construct a novel one-dimensional copper(I) polymer with η^2-olefin binding mode, *catena*-(2,2′-bipyridine)(*trans*-4-pyridylacrilic acid)copper(I) tetrafluoroborate $\{[bpy)(4\text{-}hpya)Cu(I)](BF_4)\}_n$ **1** which, to the best of our knowledge, represents the first example of a stable copper(I)–olefin complex capable of co-existing with an organic acid (Scheme 1).

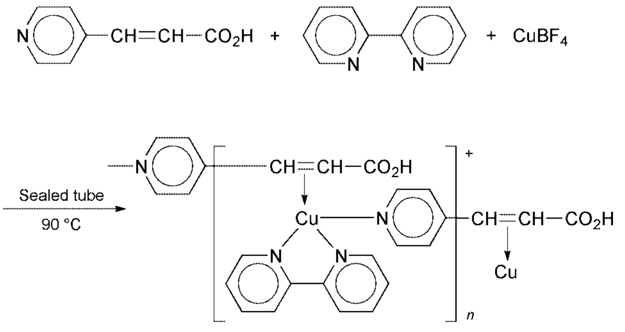
Golden yellow crystals of **1** were obtained by treating 4-hpya, bpy and $Cu(MeCN)_4(BF_4)$ under solvothermal reaction conditions.† The IR spectrum of complex **1** shows a very strong peak at 1072 cm^{-1}, indicating a typical uncoordinated BF_4^- anion. A broad peak at *ca.* 3224–3392 cm^{-1} and two peaks at 1712s and 1600m cm^{-1} suggest that the carboxylic acid group of 4-hpya in **1** is protonated.[8]

Complex **1** possesses high thermal stability, as evidenced from thermogravimetric analysis. The TGA curve of polycrystalline complex **1** showed that no weight loss occurred below *ca.* 229 °C.

The X-ray crystal analysis of complex **1**‡ revealed that Cu(I) ion in **1** is coordinated in a distorted tetrahedral geometry, which is defined by three nitrogen atoms (two from bpy and one from 4-hpya) and the C=C moiety of the olefin of 4-hpya [Fig. 1(a)]. The ligand 4-hpya acts as a neutral bidentate spacer to link two Cu(I) ions by an N atom and an olefin moiety to give rise to a 1D coordination polymer, as depicted in Fig. 1(b). The C=C bond distance [1.361(6) Å] of the coordinated olefin, is comparable to those found in $[Cu(bpy)(C_2H_4)]ClO_4$ [1.360(13)–1.346(18) Å],[3] $[Cu(phen)(C_2H_4)]\cdot ClO_4$ [1.361(22) Å],[3] $[Cu_2\{HB(3,5\text{-}Me_2pz)_3\}(C_2H_4)Cl]$ [1.347(5) Å], $[Cu(C_2H_4)(dipyridylamine)]$ [1.359(7) Å],[2] $[Cu_2(O_2CCH{=}CHCO_2)]$ [1.371(14) Å][7] and $[Bu^t{}_2P(NSiMe_3)_2\text{-}\kappa^2 N]Cu(\eta^2\text{-}C_2H_4)$ [1.362(6) Å].[6] However, it is slightly longer than those found in $[Cu\{HB(3,5\text{-}Me_2pz)_3\}(C_2H_4)]$ [1.329(9) Å][1] and $[Cu_2(cot)(hfacac)_2]$ [1.31(1)–1.33(1) Å] (cot = cycloocatatetraene, hfacac = hexafluoroacetylacetonate).[4]

Interestingly, the coordinated olefinic bond in **1** [1.361(6) Å] is longer than free ethylene [1.337(2) Å], suggesting that the coordination to copper(I) could potentially activate the olefinic bond which may be of use in catalysis.[6] The Cu–N and Cu–O bond lengths of complex **1** are normal and lie within the distances expected for Cu(I) complexes. Moreover, the Cu–C bond distances [2.058(4)–2.068(4) Å] in **1** are comparable to those found in other reported copper(I) organometallic compounds.

It is notable that in complex **1** the H atom of carboxylic acid group of 4-hpya is hydrogen-bonded to one of the fluorine atoms of BF_4^-, as shown in Fig. 1(c), while the other three fluorine atoms of BF_4^- are also weakly hydrogen-bonded to the H atoms of the pyridine ring (3.323–3.341 Å).[9] Similarly, the carbonyl oxygen is hydrogen-bonded to H atoms of pyridine ring (3.341 Å). Moreover, there are the stabilizing π–π interactions (*ca.* 3.71 Å) of adjacent strands, clearly suggesting that π–π stacking of neighboring strands plays an important role in stabilizing the copper(I)–olefin complex. Thus, overall hydrogen bonding and π–π stacking make **1** a stable 3D coordination polymer. The secondary interactions may explain why 4-hpya exists in its protonated form in complex **1**. As far as we are aware, **1** is the first example of 1D Cu(I)–olefin coordination polymer containing a protonated organic acid ligand, which is stabilized hydrogen-bonding and π–π stacking, similar to weak hydrogen bonds of the type $C\text{–}H_{aromatic}\cdots F\text{–}C$



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Scheme 1

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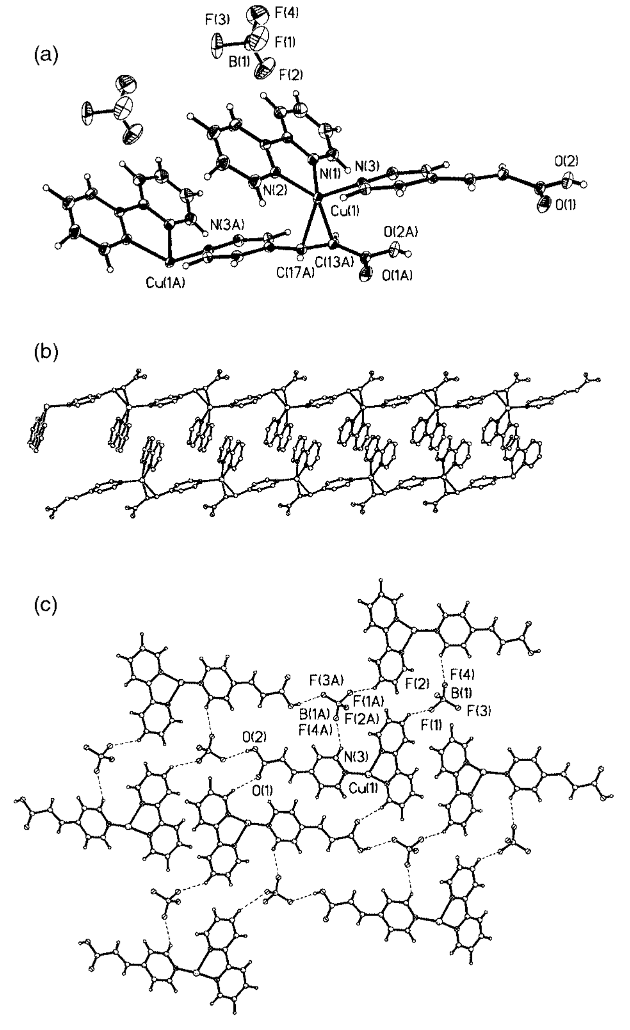

Fig. 1 (a) An ORTEP diagram of the asymmetric unit of **1** (30% ellipsoid probability). Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.097(4), Cu(1)–N(2) 1.998(4), Cu(1)–N(3) 2.041(3), Cu(1)–C(17A) 2.068(4), Cu(1)–C(13A) 2.058(4), C(13)–C(17) 1.361(6); N(1)–Cu(1)–N(2) 80.7(14), N(3)–Cu(1)–N(1) 104.78(14), C(13)–Cu(1)–C(17) 138.52(17), N(3)–Cu(1)–C(13) 102.36(15), N(2)–Cu(1)–C(13) 142.34(16). (b) An extended 1D chain representation of **1** showing π–π stacking between adjacent strands. (c) A simplified hydrogen-bonding network representation of **1**.

in organic crystalline solids capable of stabilizing the secondary structure of biomolecules such as DNA.[9,10] Attempts to synthesize neutral {[bpy)(4-pya)Cu(I)]}$_n$, were unsuccessful.

The diffuse-reflectance UV–VIS spectrum of **1** shows only a low-energy band at *ca.* 429 nm, which can be assigned to the metal-to-ligand charge transfer (MLCT) band.[11] The strong red emission spectrum of **1** in the solid state at room temperature is shown in Fig. 2, with a maximum at *ca.* 647 nm (λ_{exc} = 250 nm). A clearly bathochromic shift occurs in **1** relative to [Cu$_4$I$_4$(py)] (λ_{emax} = 580 nm)[11] and [Cu(3,4-bpyBr] (λ_{emax} = 580 nm),[11] which is probably due to π–back-donation from the filled metal D$_\pi$ orbital to the vacant antibonding π* orbital of the coordinated olefin.[1b]

In conclusion, the rational design of building blocks and the flexible combination of copper(I) in the supramolecular system provide a robust strategy for the construction of coordination polymers supported by metal–olefin bonds.

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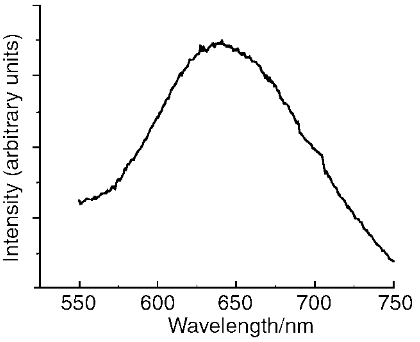

Fig. 2 Fluorescent emission spectrum of **1** in the solid state.

Notes and references

† *Compound* **1**: 1 mmol of Cu(MeCN)$_4$BF$_4$, 1 mmol of 2,2′-bpy and 1 mmol of 4-hpya were placed in a thick Pyrex tube (*ca.* 20 cm long). 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 then heated at 90 °C for two days to give pure golden rod crystals in 65% yield based on 4-hpya (Found: C, 47.24; H, 3.46; N, 9.65; Calc.: C, 47.44; H, 3.32; N, 9.22%). IR (KBr, cm^{-1}): 3392m, 3224m, 1712vs, 1600s, 1565w, 1441m, 1375m, 1281w, 1168s, 1072vs, 998msh, 830w, 762s, 735w and 595w.

‡ *Crystal data* for **1**: $C_{18}H_{15}BCuF_4N_3O_2$, M_r = 455.68, triclinic, space group, $P\bar{1}$, a = 7.425(2), b = 10.493(3), c = 12.177(3) Å, α = 108.12(3), β = 91.82(3), γ = 94.31(3)°, V = 905.0(4) Å^3, Z = 2, T = 293(2) K, D_c = 1.672 g cm^{-3}. Mo-Kα radiation (λ = 0.71073 Å), μ = 1.267 mm^{-1}, R_1 = 0.0441, wR_2 = 0.1179 for 2351 observed reflections from 3174 independent reflections, GOF = 0.976. CCDC 182/1706. See http://www.rsc.org/suppdata/cc/b0/b004001k/ for crystallographic files in .cif format.

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