[Electronic supplementary information (ESI)]

Structural diversity of copper(I) ethylene complexes with 2,4-bis(2-pyridyl)pyrimidine directed by anions

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Table S1 Crystallographic data for Cu(I)–bpprd/C_2H_4 complexes **1**–**4**

	$[Cu_2(bpprd)(\eta^2\text{-}C_2H_4)_2(ClO_4)_2]$ (**1**)	$[Cu_4(bpprd)_2(\eta^2\text{-}C_2H_4)_4(\mu\text{-}NO_3)_2](NO_3)_2$ (**2**)	$[Cu_2(bpprd)(\eta^2\text{-}C_2H_4)_2(BF_4)]BF_4$ (**3**)	$\{[Cu_6(bpprd)_4(\eta^2\text{-}C_2H_4)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2H_4)(\mu\text{-}BF_4)_2](BF_4)_4\}_n$ (**4**)
Formula	$C_{18}H_{18}Cl_2Cu_2N_4O_8$	$C_{18}H_{18}Cu_2N_6O_6$	$C_{18}H_{18}B_2Cu_2F_8N_4$	$C_{62}H_{52}B_6Cu_6F_{24}N_{16}$
Formula Weight	616.34	541.46	591.06	1923.29
Crystal System	monoclinic	triclinic	monoclinic	monoclinic
Space Group	$P2_1/c$ (No. 14)	P1(-) (No. 2)	$P2_1/c$ (No. 14)	$C2_1/c$ (No. 15)
a /Å	11.3225(3)	9.3576(3)	11.1296(4)	22.7929(6)
b /Å	13.0447(4)	10.9852(6)	12.9401(4)	11.3730(2)
c /Å	15.7577(5)	11.9635(7)	15.7337(7)	29.0946(7)
α /°	90	64.609(5)	90	90
β /°	109.276(3)	67.153(4)	109.055(4)	109.594(3)
γ /°	90	84.922(4)	90	90
V /Å	2196.91(12)	1019.33(10)	2141.78(15)	7105.3(3)
Z	4	2	4	4
D_{calc} /gcm^{-3}	1.863	1.764	1.833	1.798
F(000)	1240.0	548.0	1176.0	3824.0
μ(MoKα) /mm^{-1}	2.235	2.137	2.070	1.881
Temperature /K	100.15	100.15	97.15	97.15
Observed reflections	26013 (R_{int} = 0.0640)	19629 (R_{int} = 0.0577)	31668 (R_{int} = 0.0556)	50700 (R_{int} = 0.0281)
Refined reflections	6603 (all data); 5613 (I>2σ(I))	6011 (all data); 5130(I>2σ(I))	6502 (all data); 5816 (I>2σ(I))	10738 (all data); 9477 (I>2σ(I))
R	0.0462 (all data)	0.0396 (all data)	0.0355 (all data)	0.0408 (all data)
R_1	0.0381 (I>2σ(I))	0.0325 (I>2σ(I))	0.0306 (I>2σ(I))	0.0356 (I>2σ(I))
wR_2	0.1080 (all data)	0.0855 (all data)	0.0776 (all data)	0.0944 (all data)
GOF	1.072	1.048	1.031	1.041

R=Σ||F_o|–|F_c||/Σ|F_o|. R_1=Σ||F_o|–|F_c||/Σ|F_o| (F_o>4σ(F_o)). wR_2=[Σ(w(F_o^2–F_c^2)^2/Σw(F_o^2)^2]$^{1/2}$.

Table S2 Selected bond lengths (Å) and bond angles (°) of Cu(I)–bpprd/C_2H_4 complexes **1**–**4**

(a) $[Cu_2(bpprd)(\eta^2\text{-}C_2H_4)_2(ClO_4)_2]$ (**1**)			
Cu(1)-N(1)	1.9705(18)	Cu(1)-N(2)	2.0573(17)
Cu(1)-C(15)	2.010(2)	Cu(1)-C(16)	2.027(2)
Cu(1)-O(1)	2.573(2)	Cu(2)-N(3)	1.9988(19)
Cu(2)-N(4)	1.9990(17)	Cu(2)-C(17)	1.998(2)
Cu(2)-C(18)	2.010(2)	Cu(2)-O(7)	2.507(2)
C(15)=C(16)	1.361(3)	C(17)=C(18)	1.370(4)
N(1)-Cu(1)-N(2)	82.10(7)	N(1)-Cu(1)-C(15)	113.08(9)
N(1)-Cu(1)-C(16)	152.19(9)	N(1)-Cu(1)-O(1)	92.00(7)
N(2)-Cu(1)-C(15)	158.88(8)	N(2)-Cu(1)-C(16)	123.28(8)
N(2)-Cu(1)-O(1)	96.06(7)	C(15)-Cu(1)-C(16)	39.41(10)
C(15)-Cu(1)-O(1)	97.88(8)	C(16)-Cu(1)-O(1)	95.85(8)
N(3)-Cu(2)-N(4)	83.15(7)	N(3)-Cu(2)-C(18)	155.41(9)
N(3)-Cu(2)-C(17)	116.28(9)	N(3)-Cu(2)-O(7)	87.26(7)
N(4)-Cu(2)-C(17)	159.12(9)	N(4)-Cu(2)-C(18)	119.64(9)
N(4)-Cu(2)-O(7)	90.32(7)	C(17)-Cu(2)-C(18)	39.97(11)
C(17)-Cu(2)-O(7)	97.81(9)	C(18)-Cu(2)-O(7)	100.78(9)
(b) $[Cu_4(bpprd)_2(\eta^2\text{-}C_2H_4)_4(\mu\text{-}NO_3)_2](NO_3)_2$ (**2**)			
Cu(1)-N(1)	2.0016(14)	Cu(1)-N(2)	2.2922(13)
Cu(1)-C(15)	2.0347(16)	Cu(1)-C(16)	2.0374(17)
Cu(1)-O(1)	2.0615(12)	Cu(2)-N(3)	1.9826(14)
Cu(2)-N(4)	2.0151(13)	Cu(2)-C(17)	2.0166(17)
Cu(2)-C(18)	2.0169(17)	Cu(2)-O(2')	2.444(1)
C(15)=C(16)	1.364(3)	C(17)=C(18)	1.373(3)
N(1)-Cu(1)-N(2)	77.93(5)	N(1)-Cu(1)-C(15)	149.59(7)
N(1)-Cu(1)-C(16)	110.84(6)	N(1)-Cu(1)-O(1)	98.62(5)
N(2)-C(15)-C(15)	111.97(6)	N(2)-Cu(1)-C(16)	108.30(6)
N(2)-Cu(1)-O(1)	95.09(5)	C(15)-Cu(1)-C(16)	39.15(7)
C(15)-Cu(1)-O(1)	108.59(7)	C(16)-Cu(1)-O(1)	145.33(6)
N(3)-Cu(2)-N(4)	83.02(6)	N(3)-Cu(2)-C(17)	113.25(6)
N(3)-Cu(2)-C(18)	149.59(7)	N(3)-Cu(2)-O(2')	101.58(6)
N(4)-Cu(2)-C(17)	156.16(7)	N(4)-Cu(2)-C(18)	118.86(7)
N(4)-Cu(2)-O(2')	103.33(6)	C(17)-Cu(2)-C(18)	39.81(7)
C(17)-Cu(2)-O(2')	90.76(7)	C(18)-Cu(2)-O(2')	93.87(7)
(c) $[Cu_2(bpprd)(\eta^2\text{-}C_2H_4)_2(BF_4)]BF_4$ (**3**)			
Cu(1)-N(1)	1.9664(14)	Cu(1)-N(2)	2.0551(13)
Cu(1)-C(15)	2.0025(16)	Cu(1)-C(16)	2.0192(17)
Cu(2)-N(3)	.9894(14)	Cu(2)-N(4)	1.9967(13) . ?
Cu(2)-C(17)	1.9976(17)	Cu(2)-C(18)	2.0002(17)
Cu(2)-F(8)	2.586(2)	C(15)=C(16)	1.370(2)
C(17)=C(18)	1.368(3)		
N(1)-Cu(1)-N(2)	82.35(5)	N(1)-Cu(1)-C(15)	112.19(7)

N(1)-Cu(1)-C(16)	151.94(7)	N(2)-Cu(1)-C(15)	161.96(6)
N(2)-Cu(1)-C(16)	124.66(6)	C(15)-Cu(1)-C(16)	39.82(7)
N(3)-Cu(2)-N(4)	83.54(5)	N(3)-Cu(2)-C(17)	116.70(7)
N(3)-Cu(2)-C(18)	156.25(7)	N(3)-Cu(2)-F(8)	83.20(5)
N(4)-Cu(2)-C(17)	159.05(7)	N(4)-Cu(2)-C(18)	119.23(7)
N(4)-Cu(2)-F(8)	85.58(5)	C(17)-Cu(2)-C(18)	40.04(8)
C(17)-Cu(2)-F(8)	101.42(5)	C(18)-Cu(2)-F(8)	103.96(7)

(d) $\{[Cu_6(bpprd)_4(\eta^2\text{-}C_2H_4)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2H_4)(\mu\text{-}BF_4)_2](BF_4)_4\}_n$ (**4**)

Cu(1)-N(1)	1.9697(15)	Cu(1)-N(2)	2.1450(15)
Cu(2)-N(3)	1.9774(15)	Cu(2)-N(4)	1.9873(15)
Cu(2)-F(2)	2.543(1)	Cu(2)-C(29)	2.0130(18)
Cu(3)-N(5)	1.9222(16)	Cu(3)-N(6)	2.3470(17)
Cu(4)-N(7)	1.982(2)	Cu(4)-N(8)	2.0020(19)
Cu(4)-F(1)	2.591(1)	Cu(4)-C(30)	1.997(3)
Cu(4)-C(31)	2.004(2)	C(29)=C(29'')	1.436(2)
C(30)=C(31)	1.365(5)		
N(1)-Cu(1)-N(2)	80.77(6)	N(1)-Cu(1)-N(1')	156.61(9)
N(1)-Cu(1)-N(2')	109.96(6)	N(2)-Cu(1)-N(2')	126.97(8)
N(3)-Cu(2)-N(4)	83.99(6)	N(3)-Cu(2)-C(29'')	160.73(7)
N(3)-Cu(2)-C(29)	119.11(7)	N(4)-Cu(2)-C(29'')	115.00(7)
N(4)-Cu(2)-C(29)	156.80(7)	F(2)-Cu(2)-C(29)	96.71(6)
F(2)-Cu(2)-C(29'')	92.19(6)	F(2)-Cu(2)-N(3)	87.31(6)
F(2)-Cu(2)-N(4)	81.32(6)	C(29)-Cu(2)-C(29'')	41.82(9)
N(5)-Cu(3)-N(6)	79.91(6)	N(5)-Cu(3)-N(5')	160.82(10)
N(5)-Cu(3)-N(6')	107.68(6)	N(6)-Cu(3)-N(6')	134.67(8)
N(7)-Cu(4)-N(8)	82.53(8)	N(7)-Cu(4)-C(30)	160.82(12)
N(7)-Cu(4)-C(31)	120.93(11)	N(8)-Cu(4)-C(30)	116.56(12)
N(8)-Cu(4)-C(31)	156.04(11)	F(1)-Cu(4)-C(30)	101.3(1)
F(1)-Cu(4)-C(31)	96.97(9)	F(1)-Cu(4)-N(7)	78.52(6)
F(1)-Cu(4)-N(8)	82.52(6)	C(30)-Cu(4)-C(31)	39.89(14)

Symmetry codes. Complex **1**: (i): x, y , z. Complex **2**: (i): x, y , z; (ii(')): 1-x, 1-y , 1-z. Complex **3**: (i): x, y , z. Complex **4**: (i): x, y , z; (ii(')): 1-x, y, 3/2-z; (iii('')): 1-x, 1-y, 1-z.

Table S3 The selected dihedral angles (°) of Cu(I)–bpprd/C_2H_4 complexes **1**–**4**

Complexes	Plane 1[a]	Plane 2[a]	Dihedral angles (°)
$[Cu_2(bpprd)(\eta^2\text{-}C_2H_4)_2(ClO_4)_2]$ (**1**)	A	B	13.31
	B	C	20.40
$[Cu_4(bpprd)_2(\eta^2\text{-}C_2H_4)_4(\mu\text{-}NO_3)_2](NO_3)_2$ (**2**)	A	B	18.43
	B	C	10.76
$[Cu_2(bpprd)(\eta^2\text{-}C_2H_4)_2(BF_4)]BF_4$ (**3**)	A	B	15.42
	B	C	20.39
$\{[Cu_6(bpprd)_4(\eta^2\text{-}C_2H_4)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2H_4)(\mu\text{-}BF_4)_2](BF_4)_4\}_n$ (**4**)	A	B	13.90[b]
	B	C	24.34[b]
	A	B	15.84[c]
	B	C	25.29[c]

[a] The terminal pyridyl rings (A) and (C), and the central pyrimidine ring (B) are shown in Figs **1**-**4**, respectively.

[b] The $[Cu_3(bpprd)_2(\eta^2\text{-}C_2H_4)_2]^{3+}$ cation moiety.

[c] The $[Cu_3(bpprd)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2H_4)]^{3+}$ cation moiety.