Supplementary Information (ESI) for

Unprecedented cationic copper(I)-iodide aggregates trapped in "click" formation of anionic-tetrazolate-based coordination polymers

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Experimental Section

General. All chemicals were obtained from commercial sources and used as received. Infrared spectra were obtained in KBr disks on a Nicolet Avatar 360 FTIR spectrometer in the range of 4000–400 cm^{-1}. Photoluminescence measurements were carried out using crystalline samples, and the spectra were collected with a Perkin-Elmer LS 55 spectrofluorimeter.

Note: The syntheses for complexes **1-3** were stimulated by Sharpless's click chemistry of the syntheses of a variety of tetrazoles through [2+3] cycloaddition reactions of nitriles with azide in the presence of zinc salt as Lewis acid (Z. P. Demko, K. B. Sharpless, *J. Org. Chem.* 2001, **66**, 7945; Z. P. Demko, K. B. Sharpless, *Angew. Chem. Int. Ed*. 2002, **41**, 2110). This method has been extended to fabricate different coordination frameworks, firstly by Xiong *et al* (R.-G. Xiong, X. Xue, H. Zhao, X.-Z. You, B. F. Abrahams, Z.-L. Xue, *Angew. Chem. Int. Ed*. 2002, **41**, 3800; H. Zhao, Z.-R. Qu, H.-Y. Ye, R.-G. Xiong, *Chem. Soc. Rev*. 2008, **37**, 84).

Caution: *Tetrazolate salts and complexes of the heavy metals are heat- and shock-sensitive, especially 5-subsituted.*

Synthesis of $[Cu_2(\mu_3\text{-}I)(\mu_5\text{-}Cpta)]_n$ (1). A mixture of 0.50 mmol copper(I) iodide, 0.50 mmol sodium azide, 0.50 mmol isophthalonitrile and 5ml THF was stirred for 10 min in air and then transferred and sealed in a 15-mL Teflon-lined stainless steel reactor. The reactor was heated in an oven at 180°C for 72h, and then cooled to room temperature at a rate of $5°C{\cdot}h^{-1}$. Yellowish sheet-like crystals were collected and dried in air (Yield ~60% based on copper(I) salts). IR (KBr, cm^{-1}): 3442m, 3096w, 2233m, 1606m, 1460s, 1421s, 1352w, 1171m, 1043w, 898m,795m, 749m, 679s, 478w.

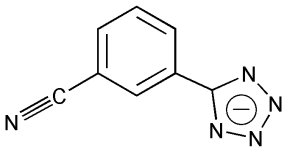
Synthesis of $[Cu_5(\mu_4\text{-}I)(\mu_4\text{-}Mtta)_3(CN)]_n$ (2). A mixture of 0.50 mmol copper(I) iodide, 0.50 mmol sodium azide and 5ml acetonitrile was stirred for 10 min in air and then transferred and sealed in a 15-mL Teflon-lined stainless steel reactor. The reactor was heated in an oven at 180°C for 72h, and

then cooled to room temperature at a rate of 5°C·h^{-1}. Brown block-like crystals were collected and dried in air (Yield ~ 60% based on copper(I) salts). IR (KBr, cm^{-1}): 3456w, 2918w, 2849w,2099m, 1632w, 1490s,1375s, 1177m, 1145s, 1048w, 700w.

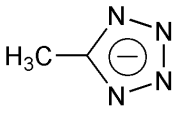
Synthesis of [Cu$_5$(μ_6-I)(μ_2-I)(μ_4-Mtta)$_3$]$_n$ (3). A mixture of 0.50 mmol copper(I) iodide, 0.50 mmol sodium azide, 5ml acetonitrile and a little THF was stirred for 10 min in air and then transferred and sealed in a 15-mL Teflon-lined stainless steel reactor. The reactor was heated in an oven at 180°C for 72h, and then cooled to room temperature at a rate of 5°C·h^{-1}. Colorless square sheet-like crystals were collected and dried in air (Yield ~50% based on copper(I) salts). IR (KBr, cm^{-1}): 3440m, 1493s, 1377s,1245w, 1186w, 1162m, 1051m,704w.

X-ray Crystallography. The crystal structures **1-3** were determined by single-crystal X-ray crystallography. Data collections were performed using a Bruker-AXS SMART CCD area detector diffractometer with Mo-Kα radiation with an ω-scan mode (λ = 0.71073Å). The structures were solved by direct methods and refined by full-matrix least squares refinements based on F^2. Multi-scan corrections were applied using SADABS. All non-hydrogen atoms were anisotropically refined. Structure solutions and refinements were performed with the SHELXL-97 package (G. M. Sheldrick, *SHELXS-97 and SHELXL-97*, Göttingen University, Göttingen, Germany, 1997).

Chart S1. *In situ* generated tetrazolate ligands via "click" reactions.



Cpta = 5-(3-cyanophenyl)-tetrazolate



Mtta = 5-methyl-tetrazolate

Scheme S1. Solvothermal syntheses of complexes **1-3**.

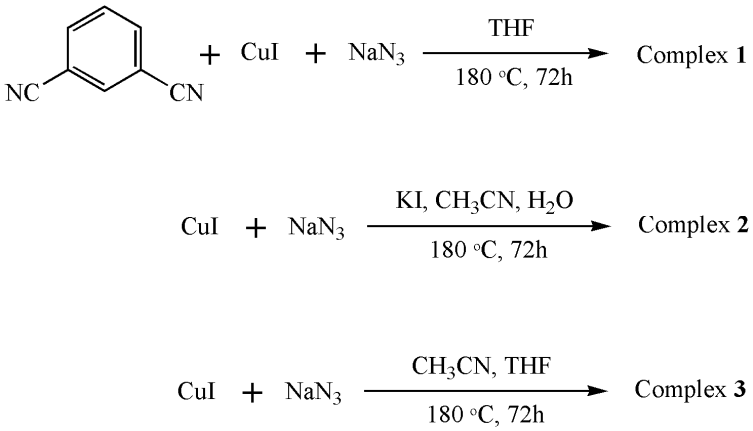


Table S1. Summary of the Crystal Data and Structure Refinement Parameters for **1-3.**

	1	**2**	**3**
Formula	$C_8H_4Cu_2IN_5$	$C_7H_9Cu_5IN_{13}$	$C_6H_9Cu_5I_2N_{12}$
Mr	424.14	719.87	820.75
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/m*	*C2/m*
a/Å	20.7315(16)	8.8201(17)	26.193(2)
b/Å	8.8557(7)	14.300(3)	8.5613(7)
c/	12.0833(10)	13.556(3)	8.2997(7)
α/°	90	90	90
β/°	110.7310(10)	92.241(3)	104.008(2)
γ/°	90	90	90
Z	8	4	4
V/Å^3	2074.8(3)	1708.5(6)	1805.8(3)
Dc/g cm^{-3}	2.716	2.799	3.019
μ/mm^{-1}	7.049	7.953	9.230
Refl. collected	12414	4572	5944
Unique refl	2368	1570	2275
R_{int}	0.0228	0.0430	0.0301
Goodness of fit	1.114	1.063	1.072
*R*1 [I>2σ(I)] [a]	0.0292	0.0360	0.0453
*wR*2 [I>2σ(I)] [b]	0.0704	0.0902	0.1297
*R*1[all data]	0.0307	0.0399	0.0506
*wR*2[all data]	0.0714	0.0951	0.1402

[a] $R1=\sum(||F_0|-|F_c||)/\sum|F_0|$; [b] $wR2=[\sum_w(F_0^2-F_c^2)^2/\sum_w(F_0^2)^2]^{1/2}$

Table S2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1-3.**

	Complex 1		
Cu(1)-N(5)	1.984(4)	Cu(1)-N(3A)	2.037(3)
Cu(1)-N(1B)	2.104(3)	Cu(1)-I(1)	2.6724(6)
Cu(2)-N(4C)	2.053(3)	Cu(2)-N(2D)	2.113(3)
Cu(2)-I(1E)	2.6276(6)	Cu(2)-I(1)	2.6656(6)
Cu(2)-Cu(2E)	2.7209(11)		
N(5)-Cu(1)-N(3A)	129.49(14)	N(5)-Cu(1)-N(1B)	95.60(15)
N(3A)-Cu(1)-N(1B)	103.99(13)	N(5)-Cu(1)-I(1)	109.51(11)
N(3A)-Cu(1)-I(1)	101.22(9)	N(1B)-Cu(1)-I(1)	118.30(9)
N(4C)-Cu(2)-N(2D)	103.86(13)	N(4C)-Cu(2)-I(1E)	116.94(9)
N(2D)-Cu(2)-I(1E)	99.07(9)	N(4C)-Cu(2)-I(1)	105.73(9)
N(2D)-Cu(2)-I(1)	112.16(9)	I(1E)-Cu(2)-I(1)	118.14(2)
	Complex 2		
Cu(1)-N(4A)	2.048(4)	Cu(1)-N(4B)	2.048(4)
Cu(1)-I(1)	2.6367(11)	Cu(1)-I(1B)	2.7186(12)
Cu(1)-Cu(1B)	2.982(2)	Cu(2)-N(1)	1.971(4)
Cu(2)-N(5)	1.971(4)	Cu(2)-N(3C)	2.097(4)
Cu(2)-I(1)	2.9512(9)	Cu(3)-N(7)	1.929(5)
Cu(3)-N(2C)	1.993(4)	Cu(3)-N(6)	2.028(4)
Cu(3)-Cu(3D)	2.8567(15)		
N(4A)-Cu(1)-N(4B)	112.3(3)	N(4A)-Cu(1)-I(1)	113.62(12)
N(4B)-Cu(1)-I(1)	113.62(12)	N(4A)-Cu(1)-I(1B)	101.84(12)
N(4B)-Cu(1)-I(1B)	101.84(12)	I(1)-Cu(1)-I(1B)	112.35(4)
N(4A)-Cu(1)-Cu(1B)	122.77(13)	N(4)-Cu(1)-Cu(1B)	122.77(13)
I(1)-Cu(1)-Cu(1B)	57.49(3)	I(1B)-Cu(1)-Cu(1B)	54.87(3)
N(1)-Cu(2)-N(5)	144.99(18)	N(1)-Cu(2)-N(3C)	103.46(17)

N(5)-Cu(2)-N(3C)	106.18(16)	N(1)-Cu(2)-I(1)	97.36(12)
N(5)-Cu(2)-I(1)	89.99(13)	N(3C)-Cu(2)-I(1)	109.48(12)
N(7)-Cu(3)-N(2C)	133.20(19)	N(7)-Cu(3)-N(6)	119.32(19)
N(2C)-Cu(3)-N(6)	102.00(17)	N(7)-Cu(3)-Cu(3D)	64.44(15)
N(2C)-Cu(3)-Cu(3D)	132.25(13)	N(6)-Cu(3)-Cu(3D)	99.23(13)
	Complex 3		
I(1)-Cu(3)	2.7626(8)	I(1)-Cu(3A)	2.7626(8)
I(1)-Cu(1A)	2.9226(7)	I(1)-Cu(1)	2.9226(7)
I(1)-Cu(2B)	2.9290(8)	I(1)-Cu(2)	2.9290(8)
I(2)-Cu(3)	2.5536(8)	I(2)-Cu(3A)	2.5536(8)
Cu(1)-N(5)	1.959(4)	Cu(1)-N(2)	1.995(4)
Cu(1)-N(1C)	2.009(4)	Cu(3)-N(6)	2.045(4)
Cu(3)-N(4D)	2.079(4)	Cu(3)-Cu(3A)	2.6706(13)
Cu(2)-N(3D)	1.927(4)	Cu(2)-N(3)	1.927(4)
Cu(2)-I(1B)	2.9290(8)		
N(5)-Cu(1)-N(2)	129.55(16)	N(5)-Cu(1)-N(1C)	118.51(17)
N(2)-Cu(1)-N(1C)	107.09(17)	N(5)-Cu(1)-I(1)	96.59(11)
N(2)-Cu(1)-I(1)	91.58(13)	N(1C)-Cu(1)-I(1)	104.55(12)
N(6)-Cu(3)-N(4D)	97.73(17)	N(6)-Cu(3)-I(2)	122.02(12)
N(4D)-Cu(3)-I(2)	119.84(11)	N(6)-Cu(3)-I(1)	100.39(11)
N(4D)-Cu(3)-I(1)	102.22(12)	I(2)-Cu(3)-I(1)	111.30(3)
N(3D)-Cu(2)-N(3)	151.8(3)	N(3D)-Cu(2)-I(1)	100.48(12)
N(3)-Cu(2)-I(1)	94.53(12)	N(3D)-Cu(2)-I(1B)	94.53(13)
N(3)-Cu(2)-I(1B)	100.48(12)	I(1)-Cu(2)-I(1B)	115.28(5)

Symmetry Codes: **1**: A x+1/2,y+1/2,z; B -x+2,y,-z+3/2; C x+1/2,-y+1/2,z+1/2, D -x+2,-y+1,-z+2; E -x+5/2,-y+3/2,-z+2; **2:** A -x,y,-z+1; B -x,-y+1,-z+1, C x+1/2,-y+1/2,z; D -x+1,y,-z+2; **3:** A x,-y,z; B -x,-y,-z+2; C -x,y,-z+1, D -x,y,-z+2.

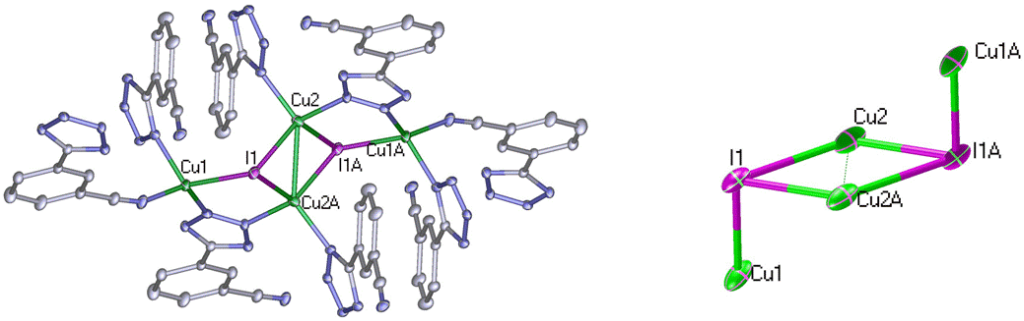


Figure S1. Coordination environments of complex **1** (left) and the cationic $(Cu_4I_2)^{2+}$ aggregate (right).

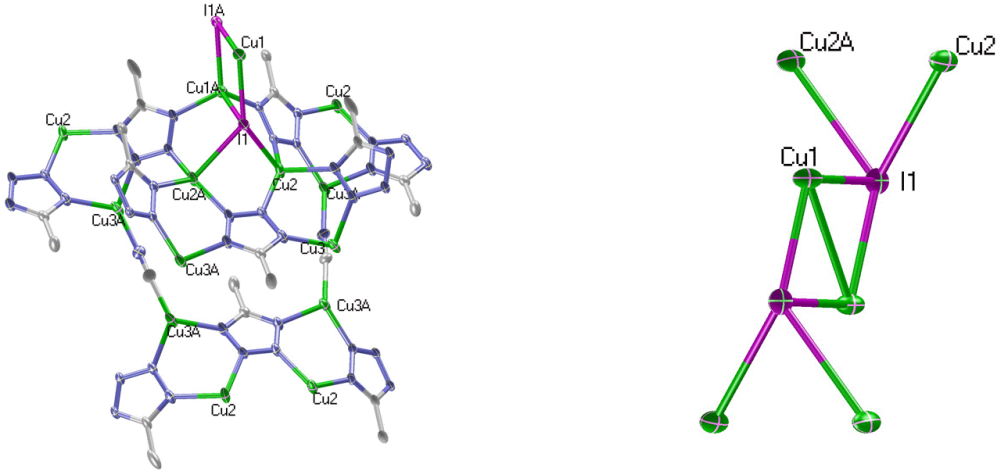


Figure S2. Coordination environments of complex **2** (left) and the cationic $(Cu_6I_4)^{2+}$ aggregate (right).

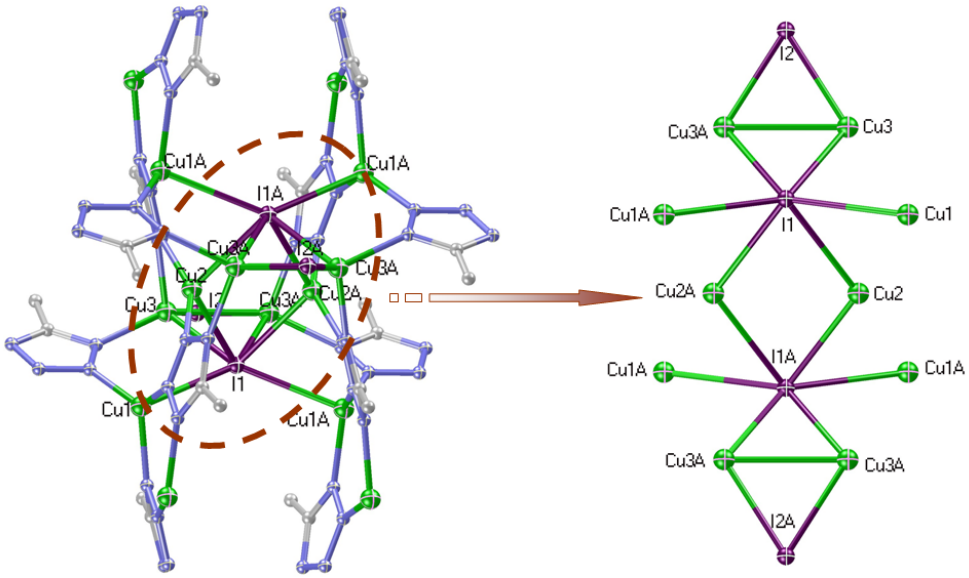


Figure S3. Coordination environments of complex **3** (left) and the cationic $(Cu_{10}I_4)^{6+}$ aggregate (right).