Supplementary Information

Substituion reactions on a hypercoordinated main-group element encapsulated in a pentacapped trigonal prismatic copper cage

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Synthesis of compounds 1–4

1. $[Cu(CH_3CN)_4](PF_6)$ (0.2987, 0.80 mmol) and $NH_4[S_2P(O^iPr)_2]$ (0.9972 g, 0.43 mmol) in 20 mL methanol at room temperature were stirred for 30 min under a nitrogen atmosphere. Further, Bu_4NBr (0.0924 g, 0.29 mmol) was added, yellow precipitate formed and the mixture solution was continuing stirred for 30 min. The yellow precipitate was collected by filtration and washed with methanol to obtain the yellow powder, $[Cu_{11}(\mu_9\text{-}Br)(\mu_3\text{-}Br)_3\{S_2P(O^iPr)_2\}_6]PF_6$. Yield: 0.13 g (74 %). Mp: 190 °C. Anal. Calcd for $C_{36}H_{84}Cu_{11}Br_4F_6O_{12}P_7S_{12}$: C, 17.71; H, 3.47; S, 15.75. Found: C, 18.04; H, 3.55; S, 15.88. $^{31}P\{^1H\}$ NMR (121MHz, $CDCl_3$): 90.7 (s, 6P), –143.0 [septet, PF_6^-, J_{PF}=712Hz], 1H NMR (300 MHz, $CDCl_3$): 4.83 (m, 3H, CH), 4.98 (m, 6H, CH), 1.41 (d, 36 H, CH_3). ESI-MS: m/z (calcd) 2298.1 (2298.0), $[Cu_{11}(\mu_9\text{-}Br)(\mu_3\text{-}Br)_3\{S_2P(O^iPr)_2\}_6]^+$; 1866.5 (1866.5), $[Cu_8(Br)\{S_2P(O^iPr)_2\}_6]^+$.

2. Compound **1** (0.3003 g, 0.1 mmol) and Bu_4NI (0.1481 g, 0.4 mmol) in 30 mL acetone were stirred at room temperature for 24 h under a nitrogen atmosphere followed by removal solvent under vacuum, leaving an yellow residue which washed with methanol solvent to give yellow powder. $[Cu_{11}(I)(\mu_3\text{-}I)_3\{S_2P(O^iPr)_2\}_6](OH)$. Yield: 0.22 g (88 %). Mp: 180 °C. Anal. Calcd for $C_{36}H_{85}Cu_{11}I_4O_{13}P_6S_{12}$: C, 17.27; H, 3.42. Found: C, 17.31; H, 3.88. $^{31}P\{^1H\}$ NMR (121MHz, $CDCl_3$): 96.16 (s, 6P). 1H NMR (300 MHz, $CDCl_3$): 4.84 (m, 6H, CH), 5.08 (m, 6H, CH), 1.36 (d, 72H, CH_3). ESI-MS: m/z(calcd) 2485.5 (2485.9), $[Cu_{11}(I)(\mu_3\text{-}I)_3\{S_2P(O^iPr)_2\}_6]^+$. In the ^{31}P NMR spectrum, no signal of PF_6^- was observed in the range of −100 to −200 ppm, indicating PF_6^- was not a counter anion. Since the isostructural species of $[Cu_{11}(\mu_9\text{-}I)(\mu_3\text{-}I)_3\{Se_2P(O^iPr)_2\}_6](OH)$ was characterized by X-ray crystallography, the anion of **2** was judged as the hydroxide.

3. Compound **1** (0.3003 g, 0.1 mmol) and $Na_2S_2O_3$ (0.0158 g, 0.1 mmol) in 30 mL acetone. About 3 h, the solvent was removed *in vacuum* and the solid washed with methanol. If the reaction time is longer than 3h, there will be an unknown brown precipitates produced. The obtained powder dissolved in CH_2Cl_2 was subjected to Al_2O_3 and silica gel column chromatography, which yielded yellow solution. After evaporation under *vacuum*, $[Cu_{11}(\mu_9\text{-}S)(\mu_3\text{-}Br)_3\{S_2P(O^iPr)_2\}_6]$, **3,** was isolated, Yield: 0.14 g (62 %). Mp: 196 °C. Anal. Calcd for $C_{36}H_{84}Cu_{11}Br_3O_{12}P_6S_{13}$: C, 19.21; H, 3.76 S,18.52. Found: C, 19.53; H, 3.92; S,18.90. $^{31}P\{^1H\}$ NMR (121MHz, $CDCl_3$): 96.4 (s, 6P), 1H NMR (300 MHz, $CDCl_3$): 4.80 (m, 3H, CH), 5.18 (m, 6H, CH), 1.36 (d, 36 H, CH_3). ESI-MS: m/z(calcd) 2271.7 (2272.0), $\{[Cu_{11}(\mu_9\text{-}S)(\mu_3\text{-}Br)_3\{S_2P(O^iPr)_2\}_6]Na\}^+$; 2169.8 (2170.1), $[Cu_{11}(\mu_9\text{-}S)(\mu_3\text{-}Br)_2\{S_2P(O^iPr)_2\}_6]^+$.

4. $[Cu_{11}(\mu_9\text{-}S)(\mu_3\text{-}I)_3\{S_2P(O^iPr)_2\}_6]$, **4,** was prepared in a similar process of **3**. Yield: 0.14 g (55 %). Mp: 193 °C. Anal. Calcd for $C_{36}H_{84}Cu_{11}I_3O_{12}P_6S_{13}$: C, 18.08; H, 3.54; S, 17.43. Found: C, 18.48; H, 3.74; S, 18.93. $^{31}P\{^1H\}$

NMR (121MHz, $CDCl_3$): 97.3 (s, 6P), 1H NMR (300 MHz, $CDCl_3$): 4.84 (m, 3H, CH), 5.08 (m, 6H, CH), 1.37 (d, 36 H, CH_3). ESI-MS: m/z(calcd) 2413.7 (2414.0), $\{[Cu_{11}(\mu_7\text{-}S)(\mu_3\text{-}I)_3\{S_2P(O^{i}Pr)_2\}_6]Na\}^+$; 2263.8 (2264.1), $[Cu_{11}(\mu_7\text{-}S)(\mu_3\text{-}I)_2\{S_2P(O^{i}Pr)_2\}_6]^+$; 2177.6 (2178.0), $[Cu_{11}(\mu_7\text{-}S)(\mu_3\text{-}I)_3\{S_2P(OiPr)_2\}_5]^+$.

Complexes **2**–**4** could also be obtained by a similar manner to that described for **1**.

Table S1. Crystallographic Data of **1**, **3** and **4**

	1	3	4
Empirical formula	$C_{36}H_{84}Br_4Cu_{11}F_6O_{12}P_7S_{12}$	$C_{36}H_{84}Br_3Cu_{11}O_{12}P_6S_{13}$	$C_{36}H_{84}Cu_{11}I_3O_{12}P_6S_{13}$
Formula weight	2443.12	2250.30	2391.27
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P(-)1	P2(1)/n	C2/c
a, Å	14.7246(4)	17.6202(4)	37.600(4)
b, Å	15.2002(4)	21.3395(5) A	17.9079(17)
c, Å	21.1551(6)	21.0229(4)	27.460(3)
α, deg	103.0220(10)	90	90
β, deg	107.1190(10)	95.7150(10)	104.703(2)
γ, deg	91.2670(10)	90	90
V, $Å^3$	4388.8(2)	7865.5(3)	17884(3)
Z	2	4	8
ρ, g cm^{-3}	1.849	1.900	1.776
μ, mm^{-1}	4.894	4.944	4.044
λ(Mo Kα), Å	0.71073	0.71073	0.71073
T, K	296(2)	296(2) K	100(2)
R_1	0.0373	0.0407	0.0351
wR_2	0.1108	0.1024	0.0843

The intensity data were collected on *Bruker APEX-II CCD* with graphite-monochromated *Mo Kα* radiation (λ = 0.71073 Å). Direct methods were used to solve the structure and to locate the heavy atoms using the *SHELXTL-97* program package. The remaining atoms were found from successive full-matrix least-squares refinements on F^2 and Fourier syntheses. All non-hydrogen atoms except C28, C29 and C30 in **1** were refined anisotropically. For **1** and **4,** the residual density located at the solvent-accessible voids cannot be modeled as solvent molecules. Thus, the SQUEEZE procedure was applied to deal with the solvent molecules. C24, C29, C30, C35 and C36 in **1** were disordered over two positions with occupancies of 0.65:0.35, 0.5:0.5, 0.5:0.5, 0.5:0.5 and 0.5:0.5, repectively. The restraints were applied to fix the bonds C28−C30, C28'−C30', C28−C29, C28'−C29', C34−C35, C34−C36, C34−C35', C34−C36', C22−C24, O10−C28, and O10−C28'. For **3**, Cu1, Cu4, Cu5, Cu6, C11 and C12 were disordered over two positions with occupancies of 0.8: 0.2, 0.8: 0.2, 0.9: 0.1, 0.7: 0.3, 0.6:0.4 and 0.6:0.4, repectively. The restraints were applied to fix the bonds C10−C11, C10−C12, C10−C11', C10−C12'. For **4**, C2, C3, C5, C6, C16, C17 and C18 were disordered over two positions with occupancies of 0.7:0.3, 0.7:0.3, 0.5: 0.5, 0.5:0.5, 0.6:0.4, 0.6:0.4 and 0.6:0.4, repectively. CCDC 943813−943815 for **1**, **3,** and **4**, respectively.

Table S2. Selected Bond Lengths (Å) for **1, 3** and **4.**

Bond	Length	Bond	Length	Bond	Length
Compound 1					
Cu1-Br1	3.0475(10)	Cu2-Br4	3.0957(10)	Cu3-Br1	3.0344(9)
Cu4-Br4	3.0681(8)	Cu5-Br1	2.9889(8)	Cu6-Br1	3.0363(9)
Br(4)-Cu(7)	2.8689(9)	Br(4)-Cu(8)	2.8138(9)	Br(4)-Cu(9)	2.8676(9)
Br(1)-Cu(3)	2.4422(9)	Br(1)-Cu(4)	2.4444(8)	Br(1)-Cu(7)	2.4077(8)
Br(2)-Cu(5)	2.4684(8)	Br(2)-Cu(6)	2.4517(9)	Br(2)-Cu(8)	2.4269(9)
Br(3)-Cu(1)	2.4282(8)	Br(3)-Cu(2)	2.4282(8)	Br(3)-Cu(9)	2.4224(9)
Compound 3					
Cu1-S13	2.4391(19)	Cu2-S13	2.4023(15)	Cu3-S13	2.4215(15)
Cu4-S13	2.4109(19)	Cu5-S13	2.5281(18)	Cu6-S13	2.806(3)
Cu7-S13	2.8704(11)	Cu8-S13	2.7686(15)	Cu9-S13	2.6546(15)
Br(1)-Cu(8)	2.4289(9)	Br(1)-Cu(6)	2.475(5)	Br(1)-Cu(5)	2.5445(15)
Br(2)-Cu(2)	2.5704(10)	Br(2)-Cu(1)	2.5715(15)	Br(3)-Cu(9)	2.4692(10)
Br(3)-Cu(9)	2.4692(10)	Br(3)-Cu(3)	2.6163(10)	Br(3)-Cu(4)	2.6261(16)
Compound 4					
Cu1-S13	2.4205(12)	Cu2-S13	2.4286(12)	Cu3-S13	2.3490(12)
Cu4-S13	2.3865(12)	Cu5-S13	2.3567(12)	Cu6-S13	2.4064(12)
Cu8-S13	2.8028(12)	Cu1-I1	2.6977(7)	Cu2-I1	2.7154(7)
Cu7-I1	2.5436(7)	Cu3-I2	2.8212(7)	Cu4-I2	2.7280(7)
Cu8-I2	2.5849(7)	Cu5-I3	2.7867(7)	Cu6-I3	2.7315(7)
Cu9-I3	2.5638(7)				

Table S3 Photophysical Data for **1–4**.

Compd.	State (T/K)	λmax/nm (ε: $M^{-1}cm^{-1}$)	$\lambda_{ex.}$ (nm)	$\lambda_{em.}$ (nm)	Stokes Shift/cm^{-1}	Life time (μs)
1	CH_2Cl_2 (298K)	343 (12000)	335	604	13000	4
	CH_2Cl_2 (77K)		332	607	13000	281
	Solid (298K)		358	627	11000	
	Solid (77K)		360	663	12000	
2	CH_2Cl_2 (298K)	380 (10000)	336	635	10000	2
	CH_2Cl_2 (77K)		320	638	10000	173
	Solid (298K)		327	617	10000	
	Solid (77K)		320	567	86000	
3	CH_2Cl_2 (298K)	369 (11000)	364	658	12000	2
	CH_2Cl_2 (77K)		335	664	14000	127
	Solid (298K)		347	670	13000	
	Solid (77K)		350	649	13000	
4	CH_2Cl_2 (298K)	376 (12000)	324	699	16000	1
	CH_2Cl_2 (77K)		365	705	13000	92
	Solid (298K)		349	655	13000	
	Solid (77K)		353	677	13000	

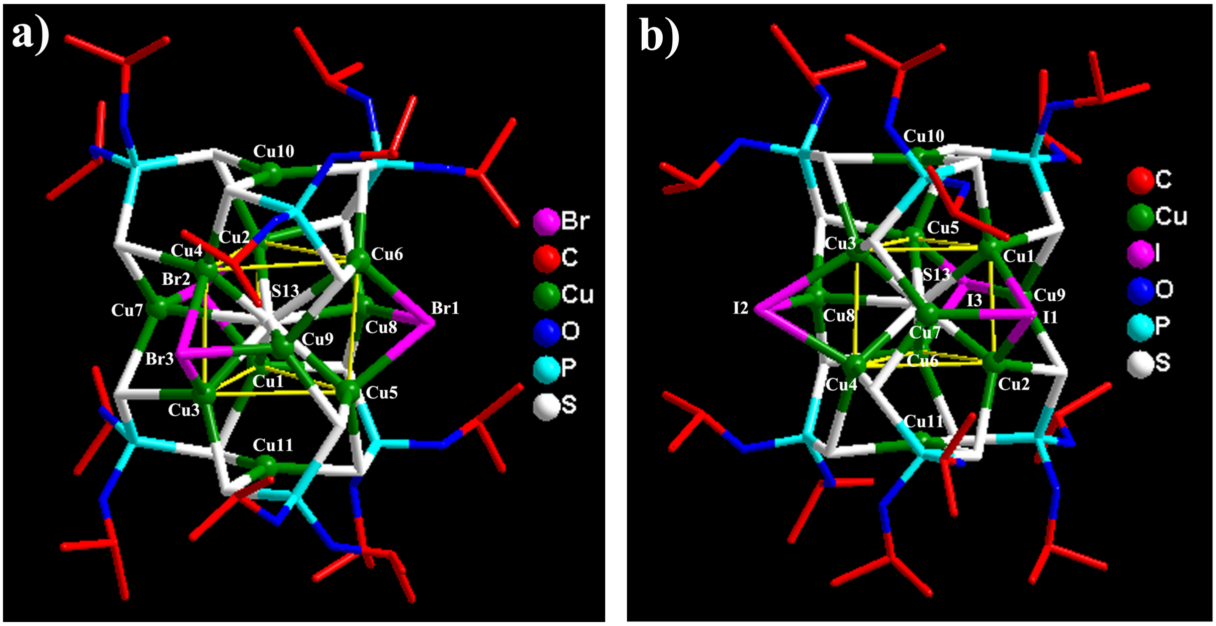

Figure S1. (a) Structure of $[Cu_{11}(\mu_9\text{-}S)(\mu_3\text{-}Br)_3\{S_2P(O^iPr)_2\}_6]$ with hydrogen atoms omitted for clarity. (b) Structure of $[Cu_{11}(\mu_7\text{-}S)(\mu_3\text{-}I)_3\{S_2P(O^iPr)_2\}_6]$ with H-atoms omitted for clarity.

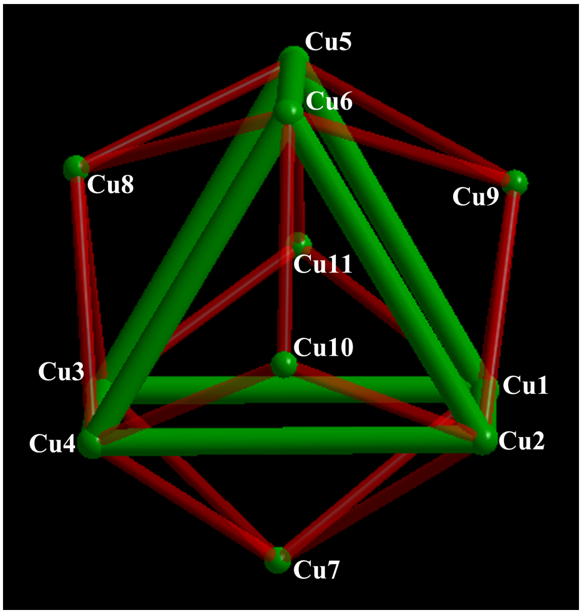

Figure S2. 3,3,4,4,4-pentacapped trigonal prism of the Cu_{11} skeleton in **1**.

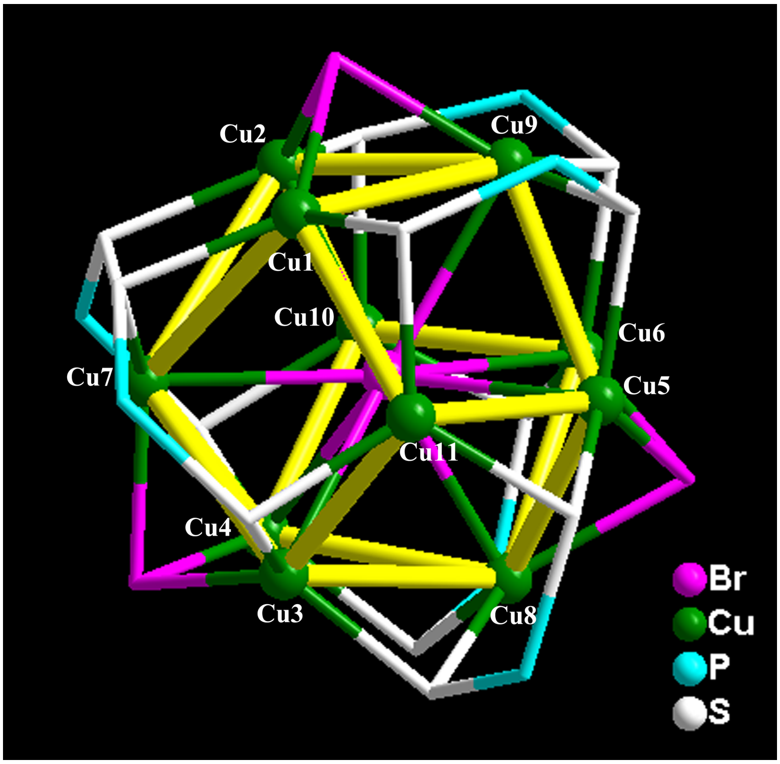

Figure S3. Structure of $[Cu_{11}(\mu_9\text{-Br})(\mu_3\text{-Br})_3\{S_2P(O^iPr)_2\}_6]^+$ with isopropoxy groups omitted for clarity. The yellow solid lines represent the edges of nine Cu_4 butterflies.