

Electronic Supplementary Material

Carboxylate Engineering for Manipulating Optical and Assembly

Properties of Copper Clusters

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Figure S1. Digital photographs of single crystals of Cu₁₄-1 cluster.



Figure S2. Digital photographs of single crystals of Cu₁₄-2 cluster.

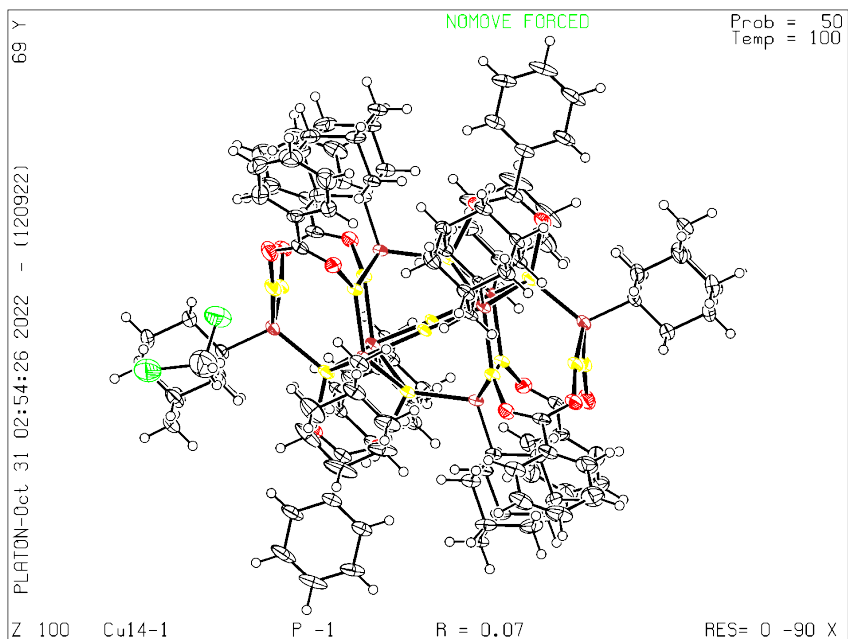


Figure S3. The thermal ellipsoids of the ORTEP diagram of Cu₁₄-1 cluster.

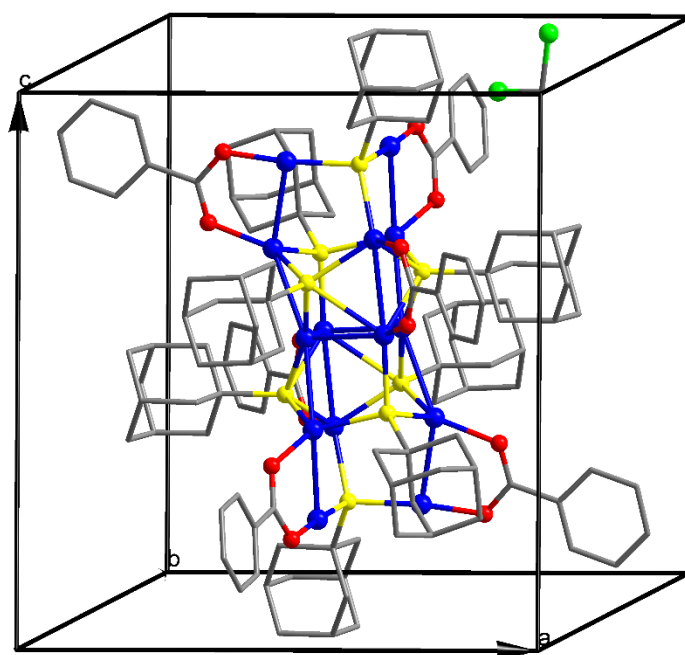


Figure S4. The packing structure of Cu₁₄-1 in the unit cell. Color codes for atoms: blue spheres, Cu; yellow spheres, S; green spheres, Cl; grey spheres, C. All hydrogen atoms are omitted for clarity.

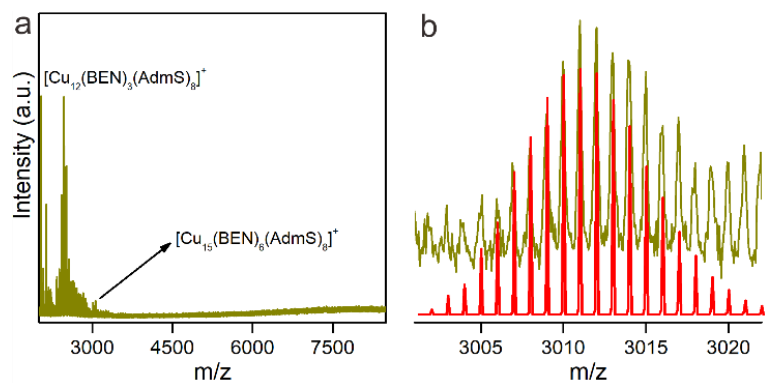


Figure S5. (a) ESI-MS of Cu₁₄-1 in the positive mode. (b) The observed (dark yellow trace) and simulated (red trace) isotopic patterns of molecular ion peak of [Cu₁₅(BEN)₆(AdmS)₈]⁺.

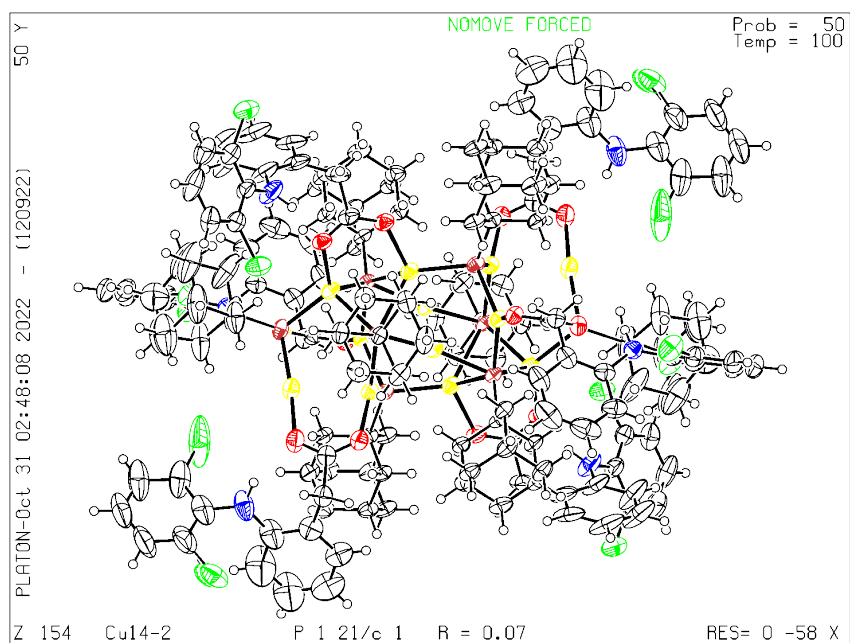


Figure S6. The thermal ellipsoids of the ORTEP diagram of Cu₁₄-2 cluster.

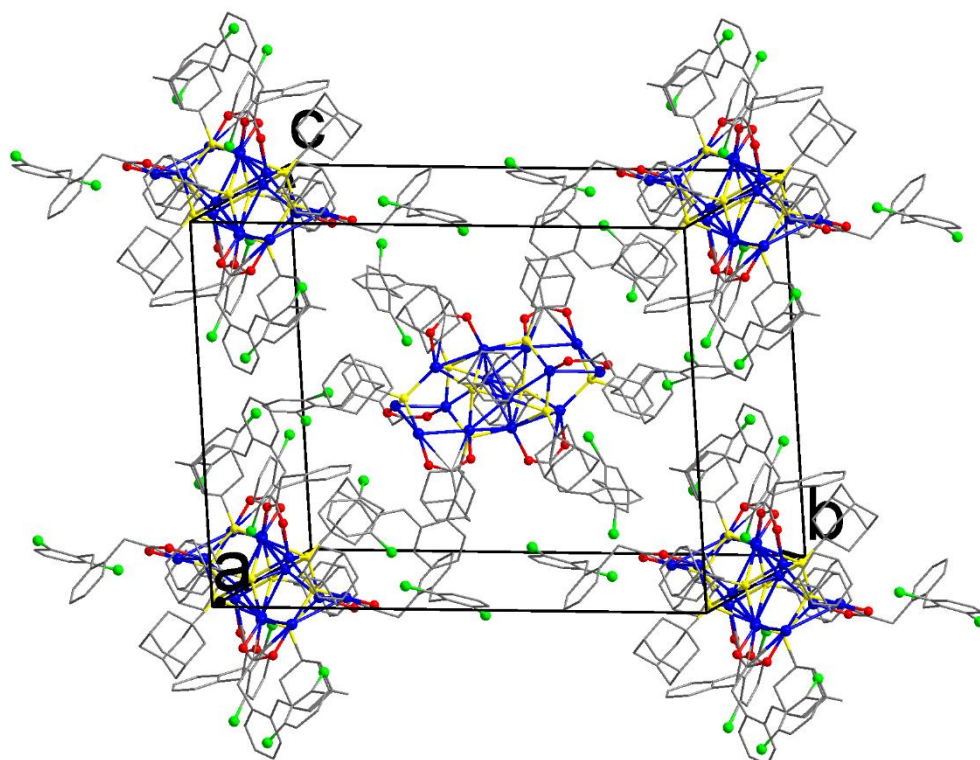


Figure S7. The packing structure of Cu₁₄-2 in the unit cell. Color codes for atoms: blue spheres, Cu; yellow spheres, S; green spheres, Cl; grey spheres, C. All hydrogen atoms are omitted for clarity.

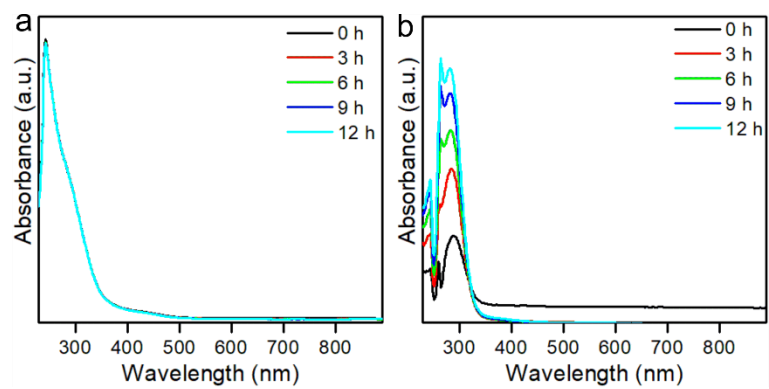


Figure S8. Time-dependent UV spectra of Cu₁₄ clusters at room temperature. (a) Cu₁₄-1. (b) Cu₁₄-2. Note: the samples were stored in air in the dark.

Table S1. Crystallographic data of Cu₁₄-1.

identification code	Cu ₁₄ -1
formula	C ₁₂₄ H ₁₅₄ C ₁₄ Cu ₁₄ O ₁₂ S ₈
formula weight	3124.30
Temperature/K	100.01(10)
crystal system	triclinic
space group	<i>P</i> 1
<i>a</i> (Å)	14.9570(4)
<i>b</i> (Å)	15.1113(4)
<i>c</i> (Å)	16.5332(5)
α (°)	65.510(3)
β (°)	87.862(2)
γ (°)	66.596(3)
<i>V</i> (Å ³)	3084.36(18)
<i>Z</i>	1
<i>D_c</i> / (g·cm ⁻³)	1.682
Radiation	Cu K α (λ = 1.54184 Å)
Theta (°) range	2.972 to 64.810
Index ranges	-13 ≤ <i>h</i> ≤ 17, -15 ≤ <i>k</i> ≤ 17, -19 ≤ <i>l</i> ≤ 19
Refls. Total	10185
restraints	0
parameters	730
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0727/0.2143
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0836/0.2195
completeness	99.79
Goof	1.094

Table S2. Crystallographic data of Cu₁₄-2.

identification code	Cu ₁₄ -2
formula	C ₁₆₄ H ₁₈₀ Cl ₁₂ Cu ₁₄ N ₆ O ₁₂ S ₈
formula weight	3998.57
Temperature/K	100.01(10)
crystal system	trigonal
space group	<i>R</i> 3
<i>a</i> (Å)	20.1767(4)
<i>b</i> (Å)	20.1767(4)
<i>c</i> (Å)	59.918(2)
α (°)	90
β (°)	90
γ (°)	120
<i>V</i> (Å ³)	21124.4(11)
<i>Z</i>	3
<i>D_c</i> / (g·cm ⁻³)	1.598
Radiation	Cu K α (λ = 1.54184 Å)
Theta (°) range	2.6760 to 64.7760
Index ranges	-13 ≤ <i>h</i> ≤ 17, -32 ≤ <i>k</i> ≤ 32, -23 ≤ <i>l</i> ≤ 23
Refls. Total	13957
restraints	84
parameters	952
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0708/0.1838
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0856/0.1958
completeness	99.94
Goof	1.067

Table S3. Comparison of average bond lengths (Å) of Cu₁₄-1 and Cu₁₄-2.

Entries	Cu-Cu	Cu-O	Cu-S
Cu ₁₄ -1	2.7557	1.955	2.2886
Cu ₁₄ -2	2.7202	1.962	2.2898

Table S4. Selected bond lengths (Å) for cluster Cu₁₄-1.

Parameter	value	Parameter	value
Cu01-Cu02	2.6688(13)	Cu04-Cu06	2.7625(14)
Cu01-Cu03	2.7254(13)	Cu04-S008	2.4753(19)
Cu01-Cu04	2.6984(13)	Cu04-S009	2.6479(19)
Cu01-Cu04	2.7638(13)	Cu04-S00A	2.2894(19)
Cu01-S008	2.1808(17)	Cu04-O00E	2.042(5)
Cu01-S009	2.1712(18)	Cu05-S00B	2.138(2)
Cu02-Cu07	2.7264(14)	Cu05-O00I	1.863(5)
Cu02-S008	2.2546(18)	Cu06-S008	2.3688(18)
Cu02-S00A	2.2380(19)	Cu06-S009	2.3376(19)
Cu02-O00H	1.988(5)	Cu06-S00B	2.284(2)
Cu03-Cu05	2.7522(14)	Cu06-O00F	1.971(5)
Cu03-S009	2.2624(18)	Cu07-S00B	2.144(2)
Cu03-S00A	2.2477(19)	Cu07-O00J	1.879(6)

Table S5. Selected bond lengths (Å) for cluster Cu₁₄-2.

Parameter	value	Parameter	value
Cu01-Cu02	2.6094(12)	Cu04-S00B	2.1486(17)
Cu01-Cu03	2.6533(12)	Cu04-O00J	1.876(4)
Cu01-Cu06	2.6238(11)	Cu05-Cu06	2.7700(13)
Cu01-Cu06	2.8163(12)	Cu05-S009	2.4193(16)
Cu01-S009	2.1901(16)	Cu05-S00A	2.3454(16)
Cu01-S00A	2.1778(16)	Cu05-S00B	2.3028(18)
Cu02-Cu04	2.7475(12)	Cu05-O00L	1.998(4)
Cu02-S008	2.2244(16)	Cu06-S008	2.2879(17)
Cu02-S009	2.2489(16)	Cu06-S009	2.5343(17)
Cu02-O00I	2.001(4)	Cu06-S00A	2.5726(17)
Cu03-Cu07	2.6991(13)	Cu06-O00K	2.026(4)
Cu03-S008	2.2077(16)	Cu07-S00B	2.1512(19)
Cu03-S00A	2.2466(17)	Cu07-O00N	1.889(5)

Reference

1. CrysAlisPro Version 1.171.35.19. (2013). Agilent Technologies Inc. Oxfordshire, OX5 1QU, UK.
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