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Crystal Structures of Benzoxazolyl-Copper(III, II, I) Complexes and Cu(II)-Mediated Aryl Carbon-Hydrogen Bromination

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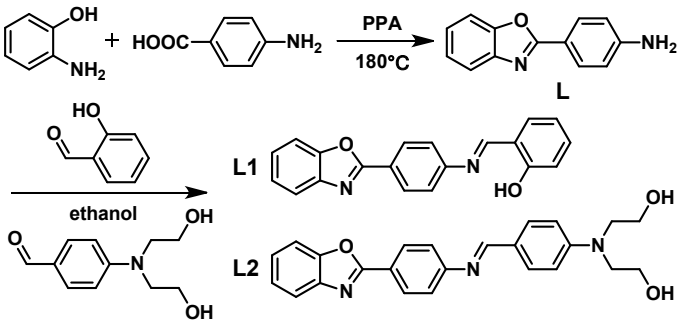


Scheme S1. The synthetic routes of ligand **L**, **L1** and **L2**.

Table S1. Selected bond lengths (Å) and angles (°) for **1**–**3**.

$C_{26}H_{16}Br_7CuN_4O_2$ (1)					
Br(7)-C(23)	1.896(8)	Br(5)-C(10)	1.906(8)	Br(4)-C(12)	1.907(8)
Br(6)-C(25)	1.898(8)	Cu(1)-N(1)	1.997(6)	Cu(1)-Br(1)	2.3397(15)
Cu(1)-Br(2)	2.3707(19)	Cu(1)-Br(3)	2.420(2)	N(1)-Cu(1)-Br(1)	151.3(2)
N(1)-Cu(1)-Br(2)	92.05(19)	Br(1)-Cu(1)-Br(2)	96.91(6)	N(1)-Cu(1)-Br(3)	91.1(2)
Br(1)-Cu(1)-Br(3)	96.17(7)	Br(2)-Cu(1)-Br(3)	146.41(7)		
$C_{13}H_8Br_3CuN_2O$ (2)					
Br(1)-Cu(1)#1	2.392(2)	Br(1)-Cu(1)	2.411(2)	Br(2)-C(10)	1.894(4)
Br(3)-C(12)	1.893(4)	Cu(1)#1-Br(1)-Cu(1)	114.64(7)	N(1)-Cu(1)-Br(1)#2	125.07(11)
N(1)-Cu(1)-Br(1)	119.82(12)	Br(1)#2-Cu(1)-Br(1)	114.64(7)		
$C_{26}H_{18}Br_4CuN_4O_2$ (3)					
Cu(1)-N(1)	1.983(7)	Cu(1)-N(1)#3	1.983(7)	Cu(1)-Br(1)#3	2.4266(15)
Cu(1)-Br(1)	2.4266(15)	Br(2)-C(10)	1.896(9)	N(1)-Cu(1)-N(1)#3	180.000(1)
N(1)-Cu(1)-Br(1)#3	89.9(2)	N(1)#3-Cu(1)-Br(1)#3	90.1(2)	N(1)-Cu(1)-Br(1)	90.1(2)
N(1)#3-Cu(1)-Br(1)	89.9(2)	Br(1)#3-Cu(1)-Br(1)	180.0		
[a]Symmetry transformations used to generate equivalent atoms: #1: x-1, y, z ; #2: x+1, y, z ; #3: -x+2, -y+1, -z+1.					

Table S2. intermolecular and intramolecular bond lengths (Å) and angles (°) for **1**–**3**.

D-H···A	*d*(D-H) Å	*d*(D-A) Å	*d*(H···A) Å	∠DHA °
$C_{26}H_{16}Br_7CuN_4O_2$ (1)				
C13-H13···N1	0.930(.008)	3.067(.011)	2.837(.007)	95.41(0.51)
C26-H26···N3	0.930(.009)	2.995(.011)	2.731(.007)	97.32(0.56)
C22-H22···O2	0.930(.009)	2.784(.010)	2.477(.005)	99.38(0.52)
N2-H2A···Br4	0.860(.008)	3.075(.008)	2.651(.001)	111.72(0.53)
N2-H2B···Br5	0.860(.008)	3.100(.008)	2.665(.001)	112.68(0.52)
N4-H4A···Br6	0.860(.008)	3.069(.008)	2.634(.001)	112.64(0.52)
N4-H4B···Br7	0.860(.008)	3.092(.008)	2.653(.001)	112.99(0.52)
C9-H9···O1	0.930(.008)	2.770(.010)	2.440(.006)	100.81(0.52)
N2-H2B···Br1	0.860(.008)	3.491(.008)	2.732(.001)	147.94(0.53)
N2-H2A···Br2	0.860(.008)	3.448(.008)	2.826(.002)	130.60(0.52)
C5-H5···Br1	0.930(.009)	3.644(.009)	2.825(.001)	147.53(0.54)
N4-H4B···Br3	0.860(.008)	3.665(.008)	2.908(.001)	147.91(0.52)

$C_{13}H_8Br_3CuN_2O$ (2)				
C9-H9···O1	0.930(.004)	2.724(.006)	2.380(.003)	101.62(0.29)
C13-H13···N1	0.930(.004)	3.051(.006)	2.804(.004)	96.40(0.28)
N2-H2A···Br2	0.860(.004)	3.080(.004)	2.649(.001)	112.31(0.27)
N2-H2B···Br3	0.860(.004)	3.052(.004)	2.610(.001)	113.06(0.26)
C3-H3···O1	0.930(.006)	3.503(.007)	2.771(.003)	136.35(0.35)
N2-H2A···Br3	0.860(.004)	3.692(.004)	2.888(.001)	156.45(0.26)
N2-H2B···Br1	0.860(.004)	3.805(.007)	3.045(.003)	148.49(0.26)
C10-Br2···Br3	1.893(.004)	4.146(.004)	3.497(.004)	95.96(0.27)
$C_{26}H_{18}Br_4CuN_4O_2$ (3)				
C13-H13···N1	0.930(.009)	3.029(.013)	2.766(.008)	97.39(0.63)
N2-H2B···Br2	0.860(.008)	3.092(.010)	2.664(.002)	112.13(0.54)
N2-H2A···Br1	0.860(.009)	3.610(.010)	2.767(.002)	166.96(0.54)
C9-H9···O1	0.930(.011)	2.740(.012)	2.415(.006)	100.39(0.63)

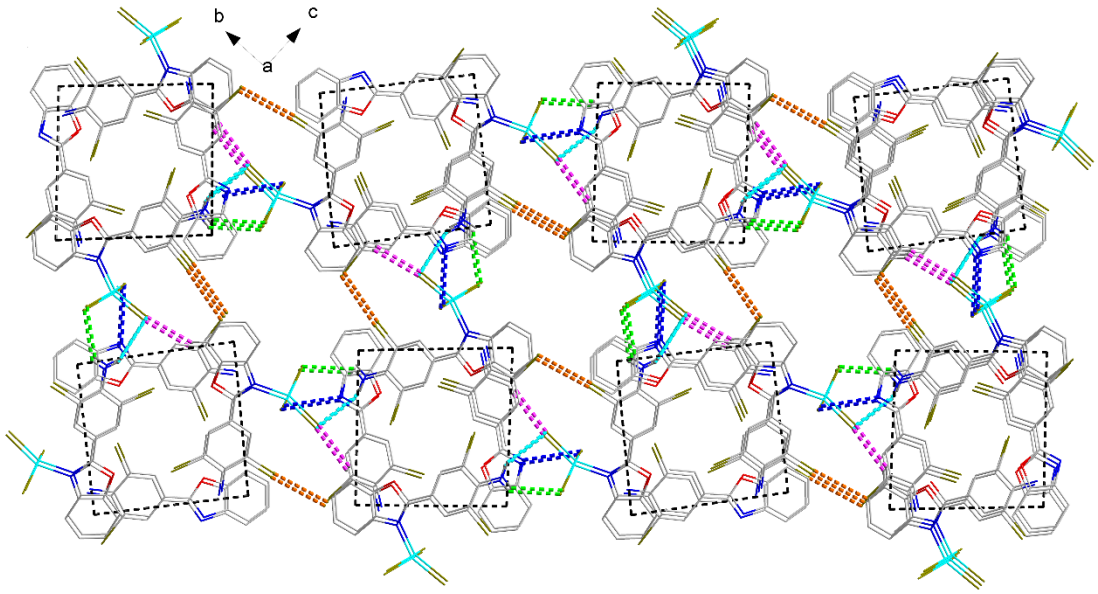


Figure S1. The three dimensional latticed supramolecular structure of **1** along the [100] direction. The colorized dotted lines represent the weak interactions and hydrogen atoms not participating in hydrogen bonds are omitted for clarity.

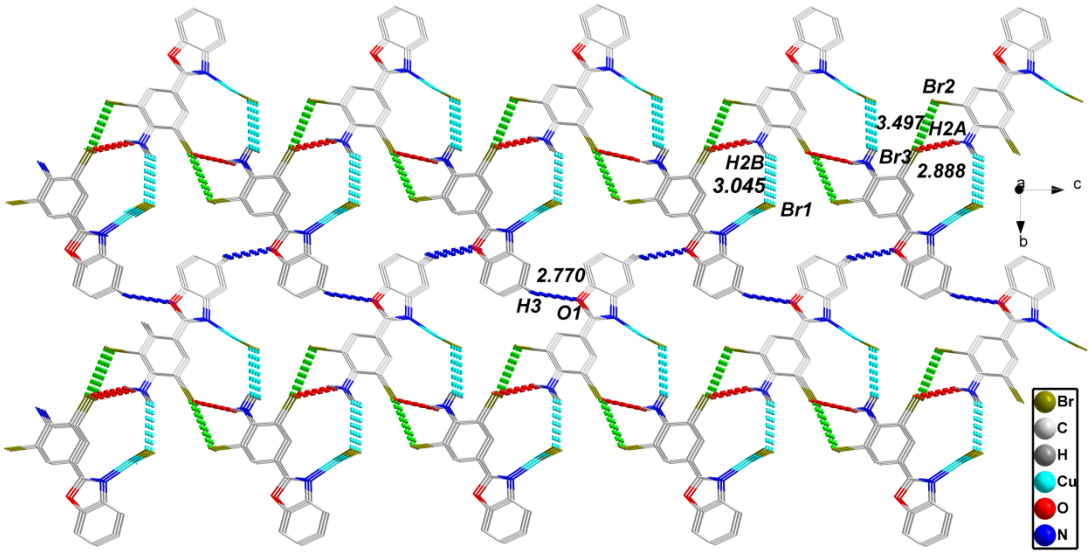
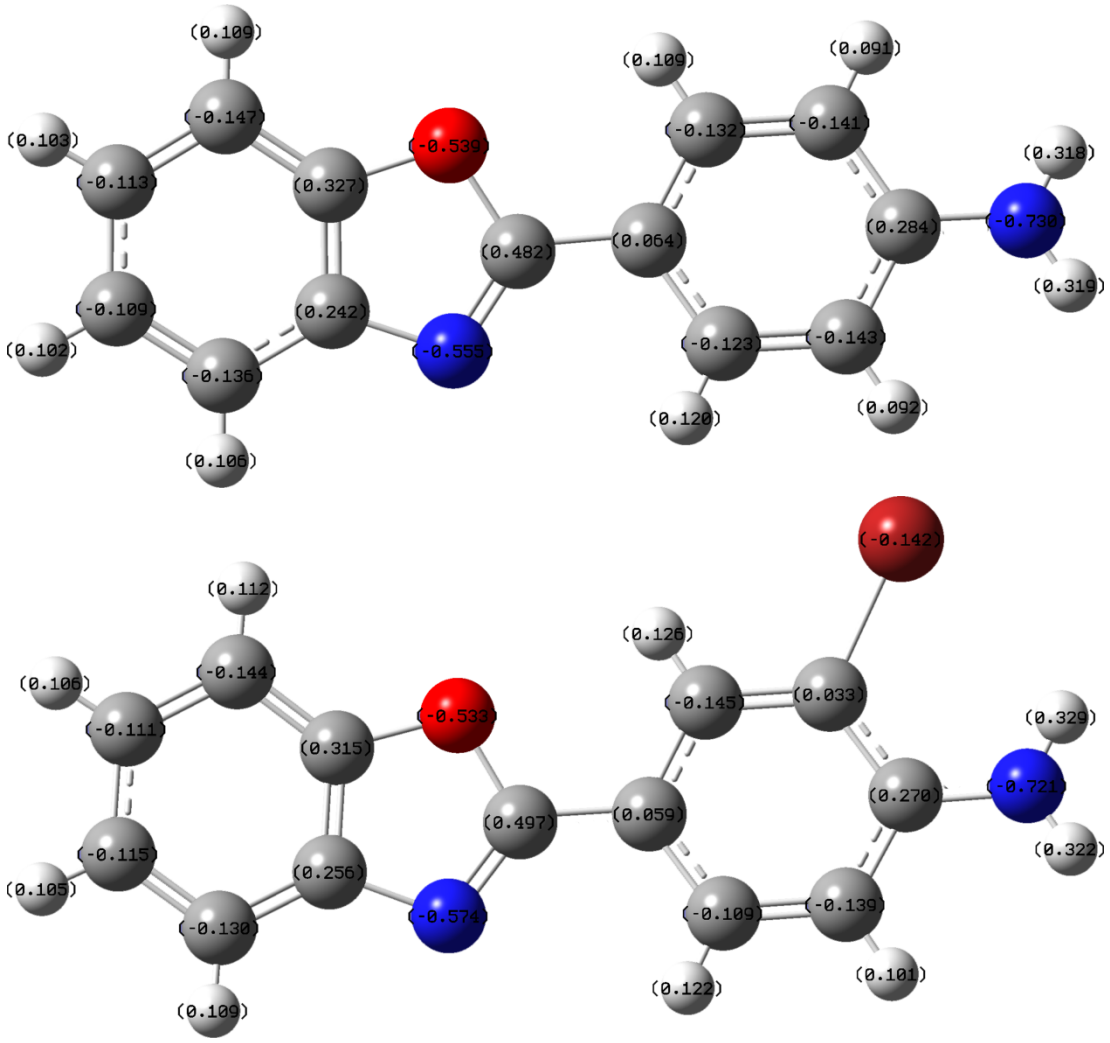


Figure S2. The three dimensional network structure of **2** formed by multiple N-H···Br, C-H···O, Br···Br weak interactions. The colorized dotted lines represent the weak interactions and hydrogen atoms not participating in hydrogen bonds are omitted for clarity.



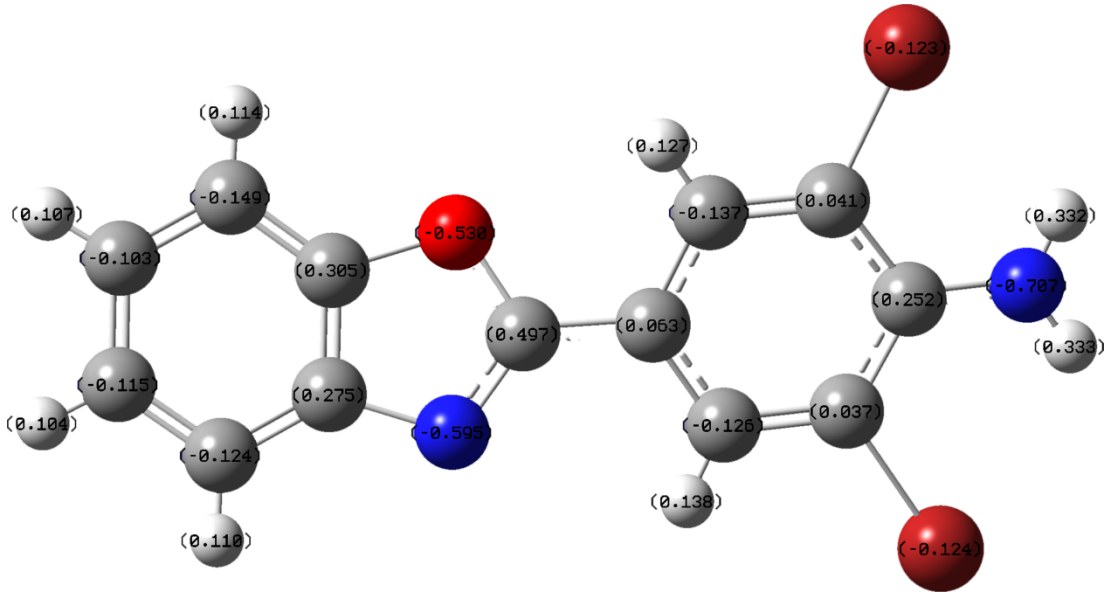


Figure S3. The Mulliken charge distribution of atoms in different ligands.

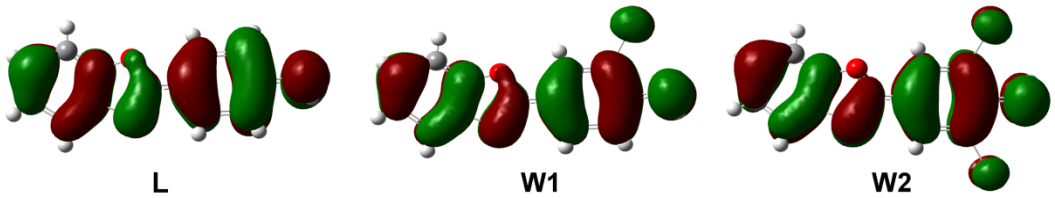


Figure S4. The Mulliken charge distribution of different ligands in the ground state.