Supporting information

Probing the Nature of Intramolecular (*sp3*)C-H···Cu(I) Interactions in Organo Thione Copper(I) Cages

Girbide Amitkumar Ramakant[#,a], Gopendra Muduli[#,a], Rakesh Kumar Rai, and Ganesan Prabusankar*[,a]

[a] Girbide Amitkumar Ramakant, Mr. Gopendra Muduli, Mr. Rakesh Kumar Rai, and Prof. Ganesan Prabusankar, Organometallics, and Materials Chemistry Lab, Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi, Sangareddy, Telangana, India-502285 E-mail: prabu@chy.iith.ac.in

[#]Equal contribution

Table of Content	
Figure S1. ^{1}H NMR spectrum of $\mathbf{L^1}$ in $CDCl_3$ at 25 °C	3
Figure S2. ^{13}C NMR spectrum of $\mathbf{L^1}$ in $CDCl_3$ at 25 °C	4
Figure S3. FT-IR spectrum of $\mathbf{L^1}$ at 25 °C	5
Figure S4. ^{1}H NMR spectrum of **1** in DMSO-d_6 at 25 °C	6
Figure S5. ^{13}C NMR spectrum of **1** in DMSO-d_6 at 25 °C	7
Figure S6. ^{1}H NMR spectrum of **2** in DMSO-d_6 at 25 °C	8
Figure S7. ^{13}C NMR spectrum of **2** in DMSO-d_6 at 25 °C	9
Figure S8. ^{1}H NMR spectrum of 2 in DMSO-d_6 at variable temperature.	10
Figure S9. FT-IR spectrum of **1** at 25 °C	11
Figure S10. FT-IR spectrum of **2** at 25 °C	12
Figure S11. FT-IR spectrum of L^1S, 1 and 2 at 25 °C.	
Figure S12. HAR-refined molecular structure of 2 with the PBE/def2-TZVPP model at full resolution 120 K.	14
Figure S13. Fourier difference electron density maps showing the electron density associated with the H-atom and Cu-atom in Cu…H-C interaction at 120 K.	15
Table S1: The structural parameters of **1** and **2**.	16
Table S2: The structural parameters of **1** and **2** at 120K	17
Table S3: Selective bond lengths and bond angles of **2** at 120K (H atoms anisotropic refinement using NoSpherA2 in Olex2).	10
Computational Methods	19
Table S4: Optimized Cartesian Co-ordinates of **2** (Cartesian coordinates of the optimized structures (in Å).	20

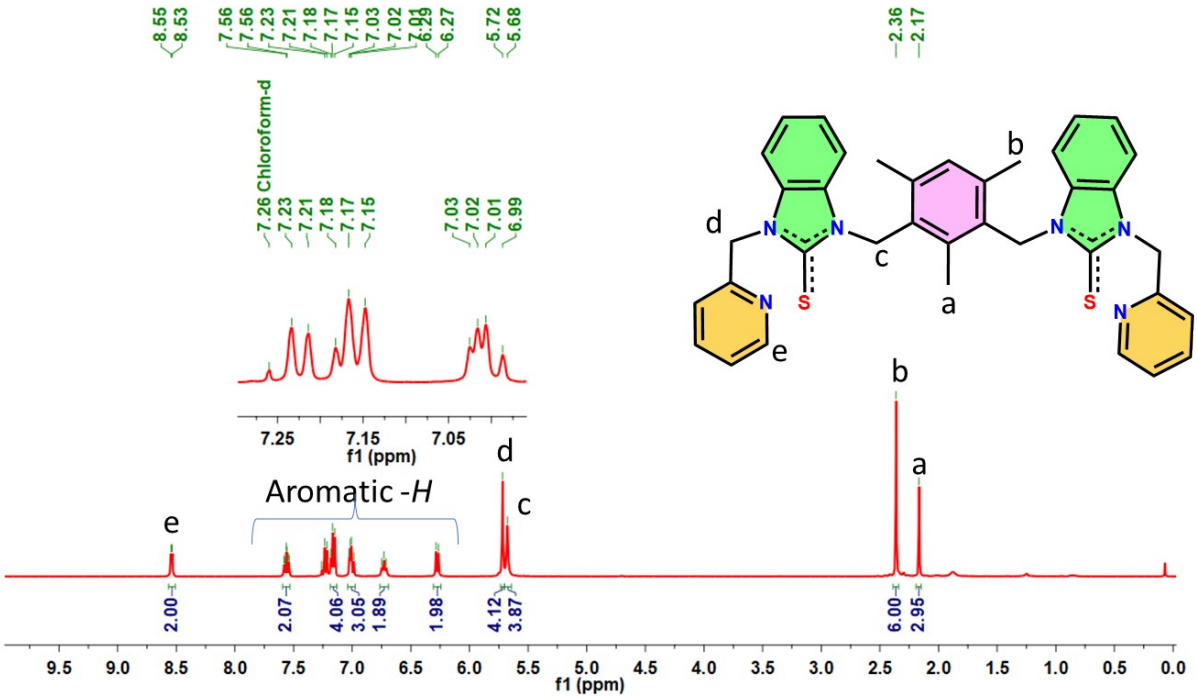

Figure S1. ^{1}H NMR spectrum of **L^{1}** in $CDCl_3$ at 25 °C

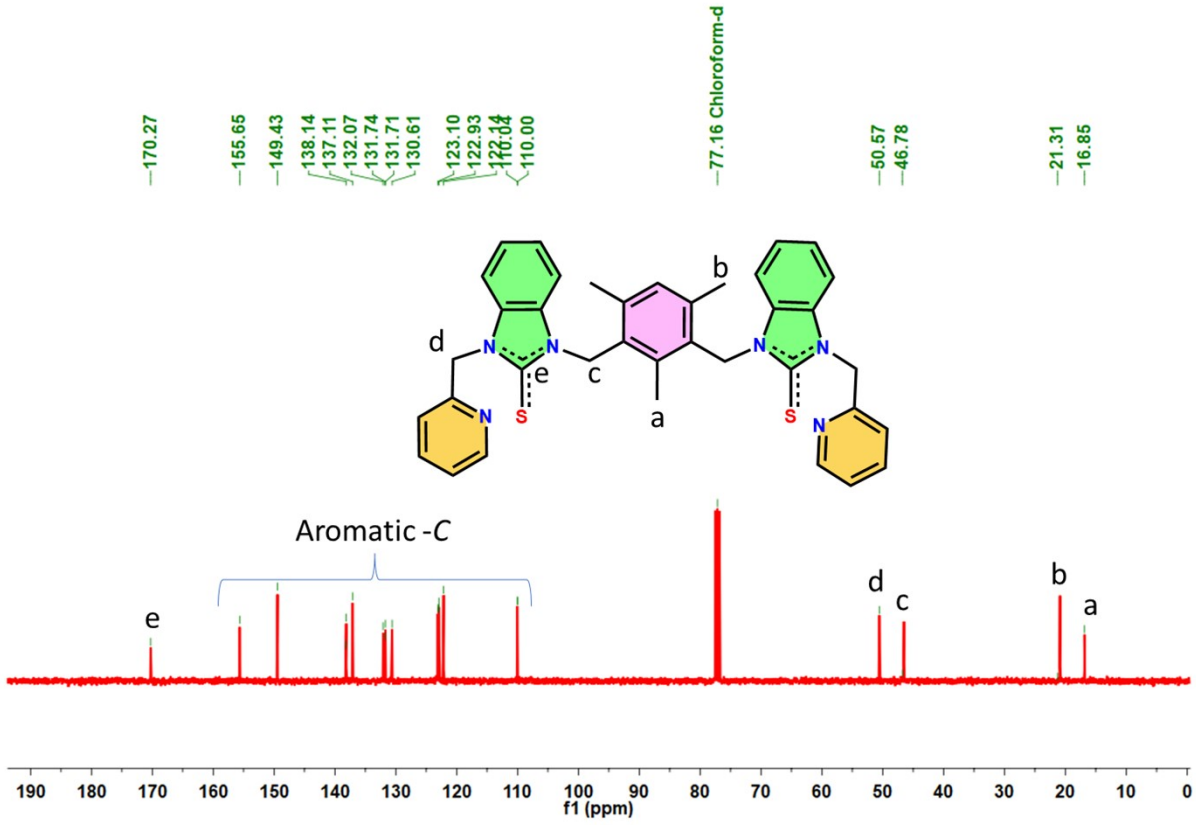

Figure S2. ^{13}C NMR spectrum of $\mathbf{L^1}$ in $CDCl_3$ at 25 °C.

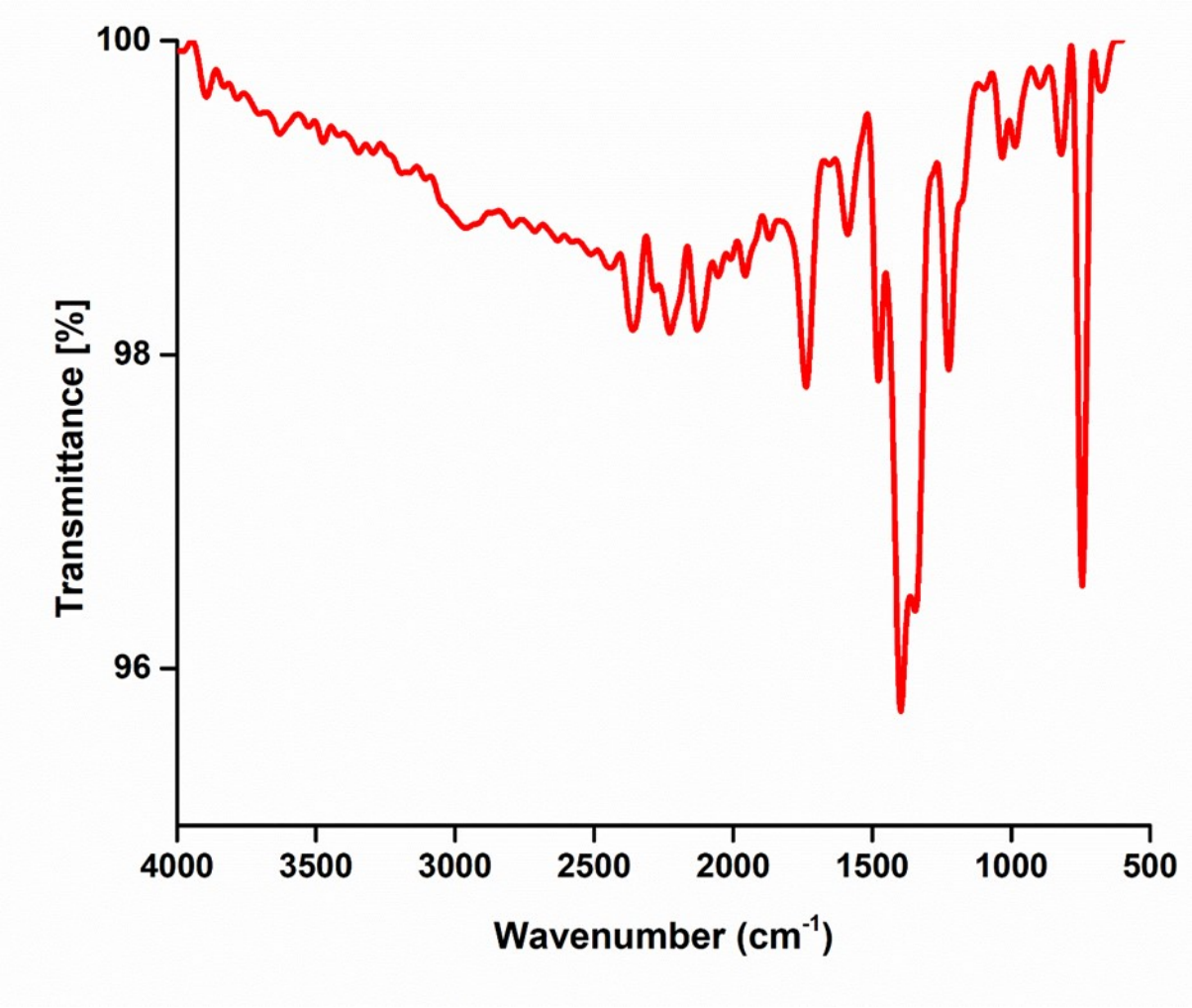

Figure S3: FT-IR spectrum of $\mathbf{L^1}$ at 25 ^{o}C.

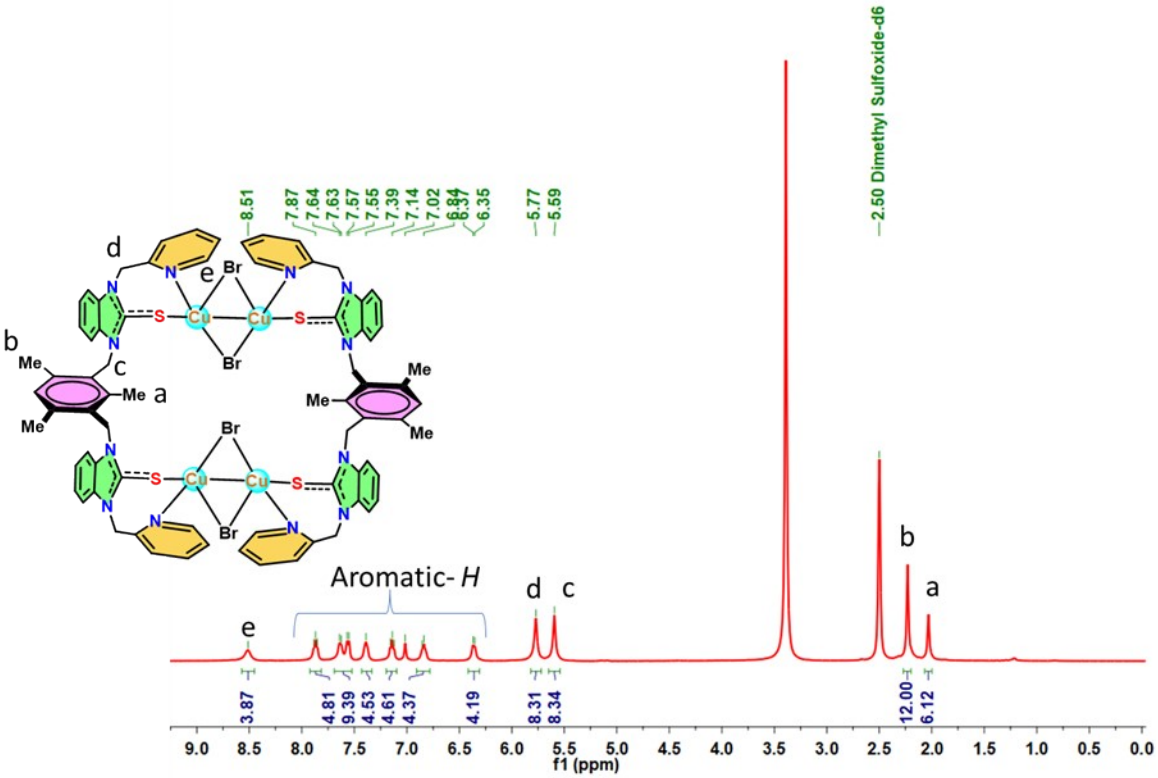

Figure S4. ^{1}H NMR spectrum of **1** in DMSO-d_6 at 25 °C.

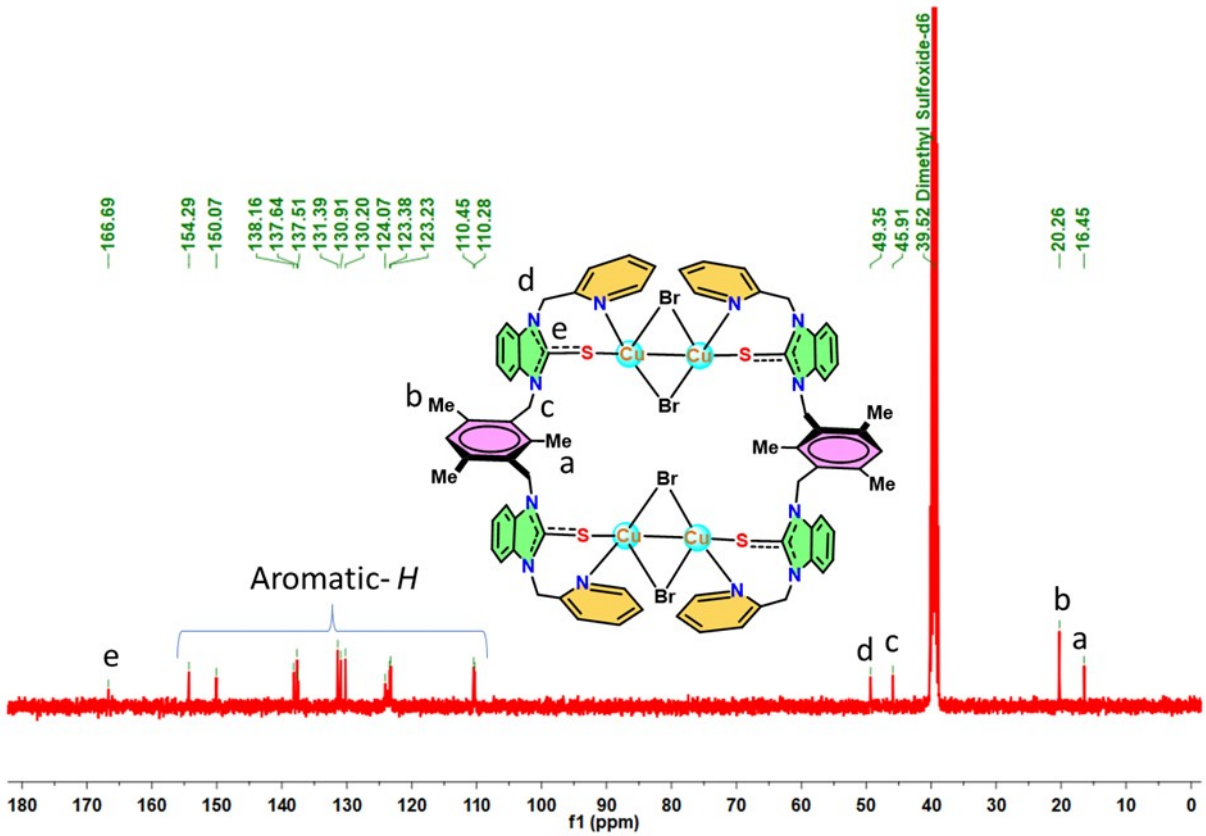

Figure S5. ^{13}C NMR spectrum of **1** in DMSO-d_6 at 25 °C

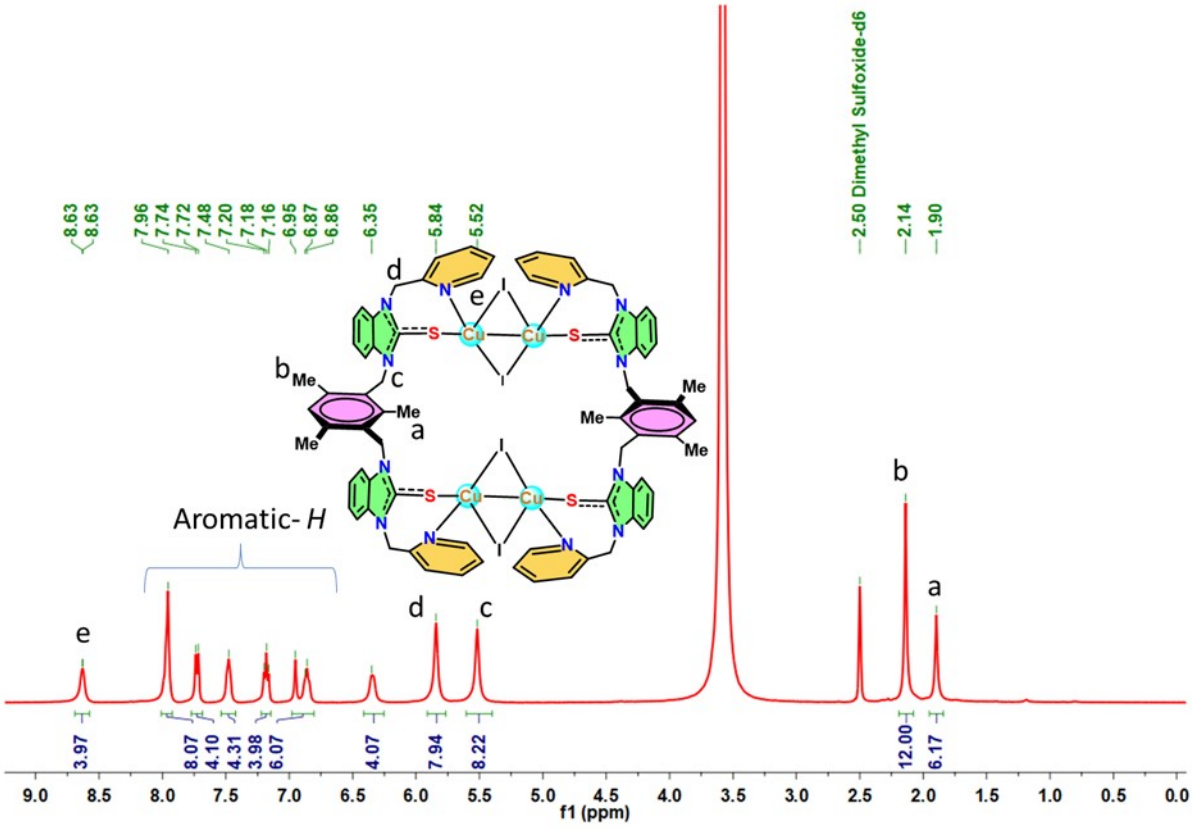

Figure S6. ^{1}H NMR spectrum of **2** in DMSO-d_6 at 25 °C.

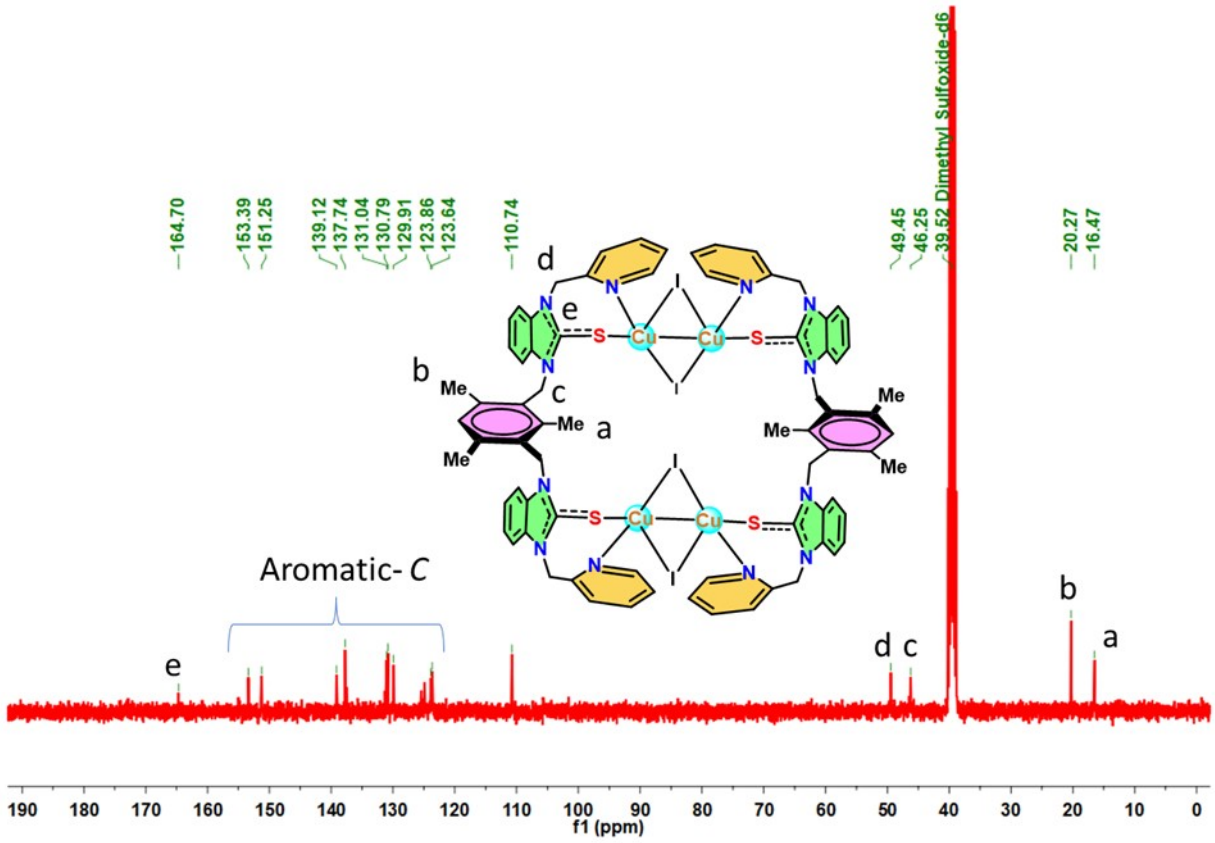

Figure S7. ^{13}C NMR spectrum of **2** in DMSO-d_6 at 25 °C.

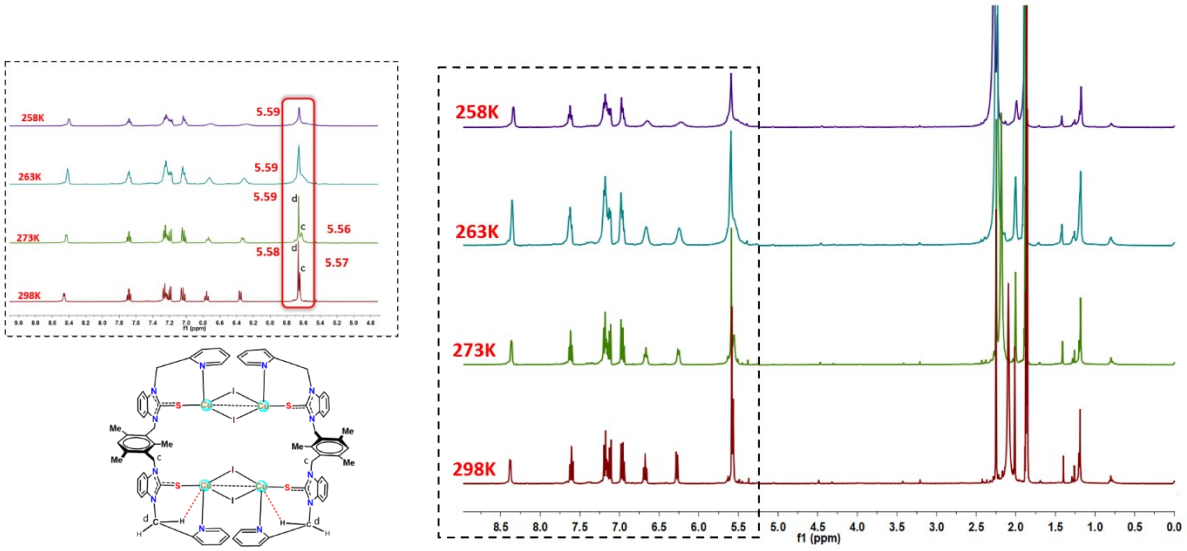

Figure S8. ^{1}H NMR spectrum of **2** in CD_3CN at variable temperatures (258, 263,273, and 298K).

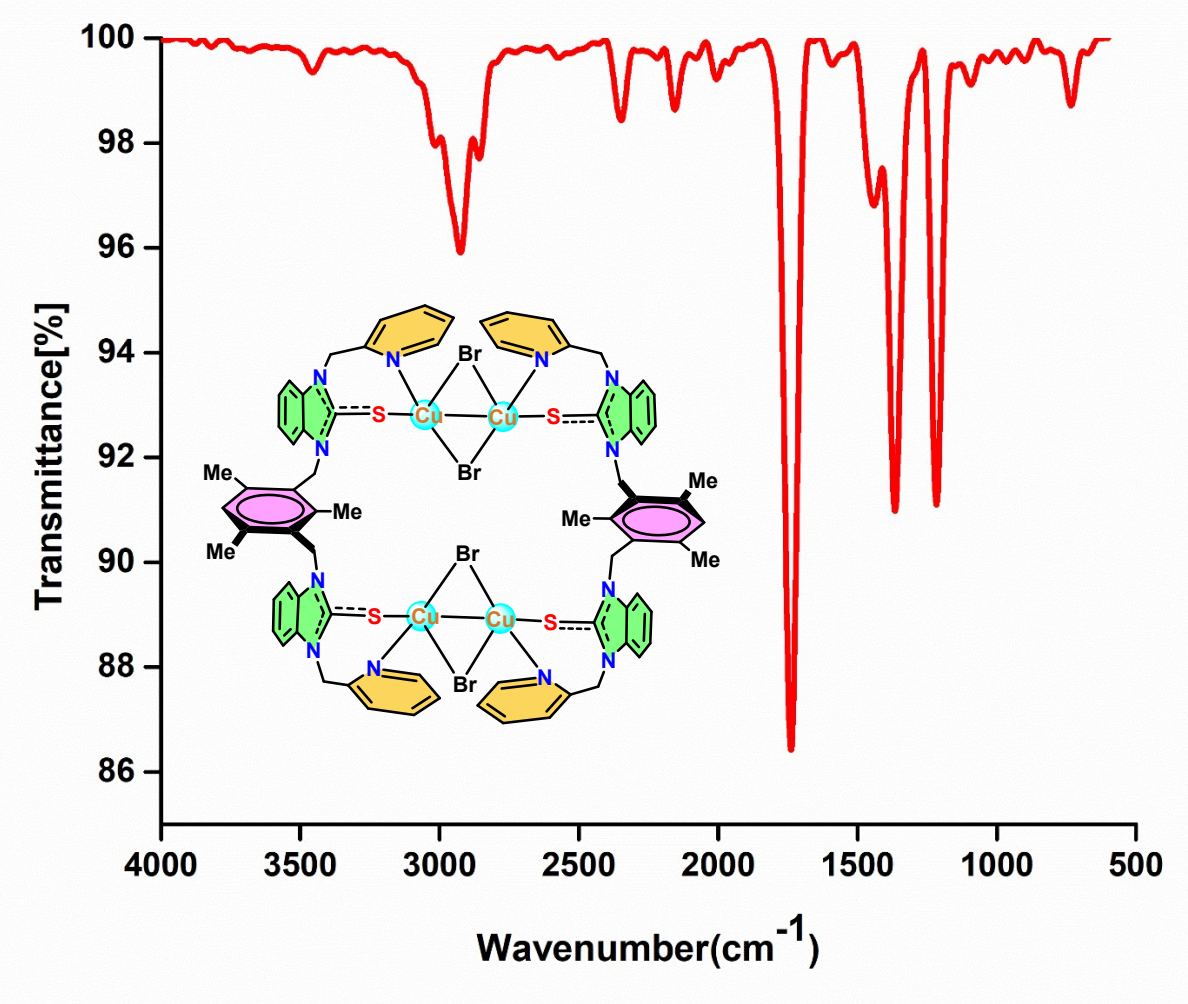

Figure S9. FT-IR spectrum of **1** at 25 °C.

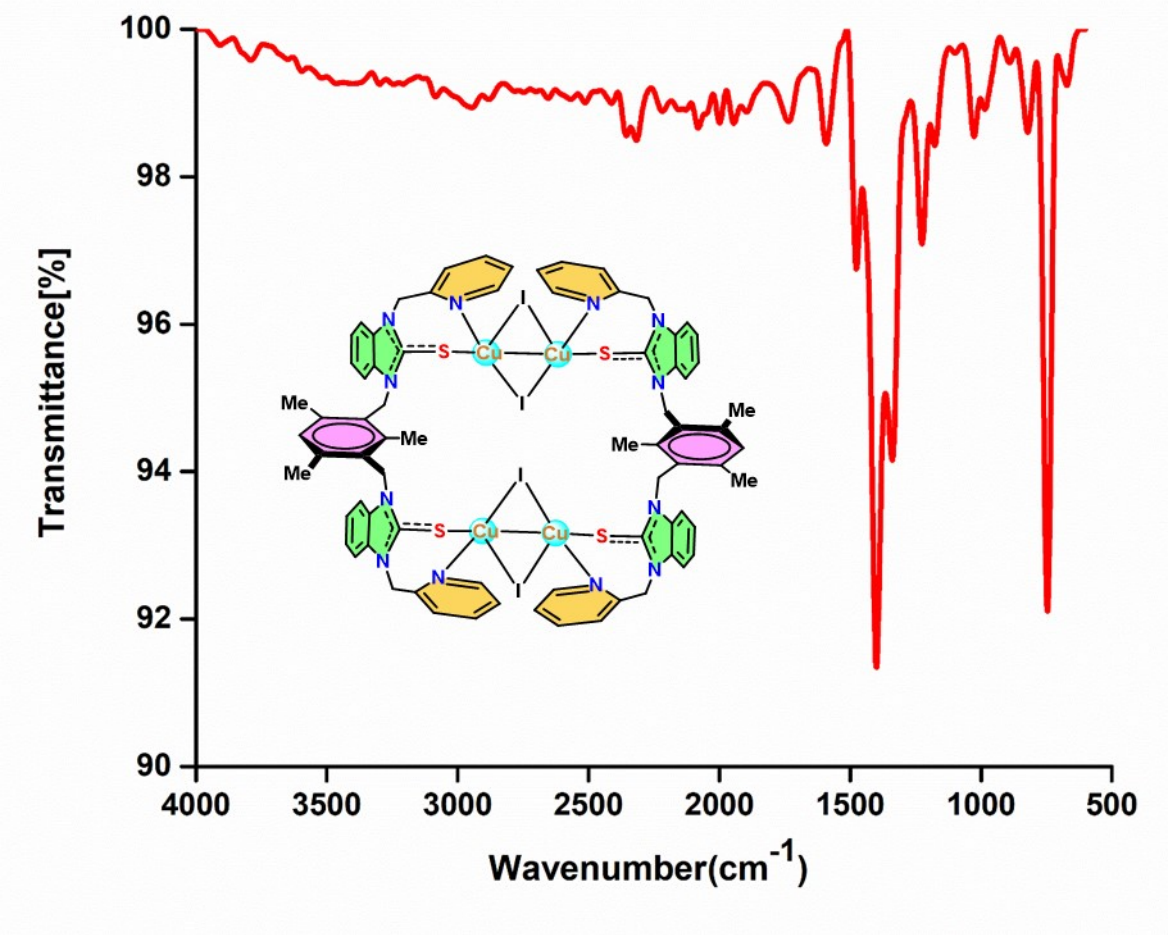

Figure S10. FT-IR spectrum of **2** at 25 °C.

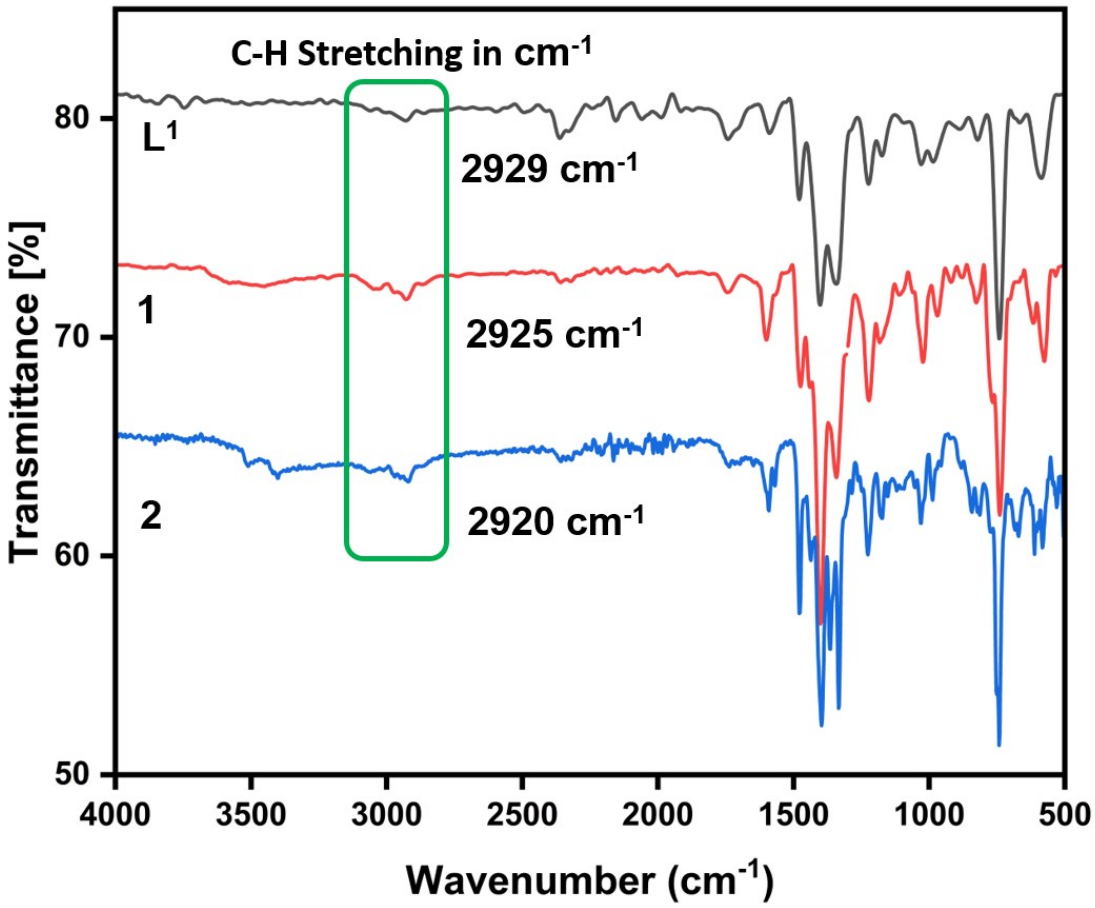

Figure S11. FT-IR spectrum of **L**[1], **1** and **2** at 25 °C.

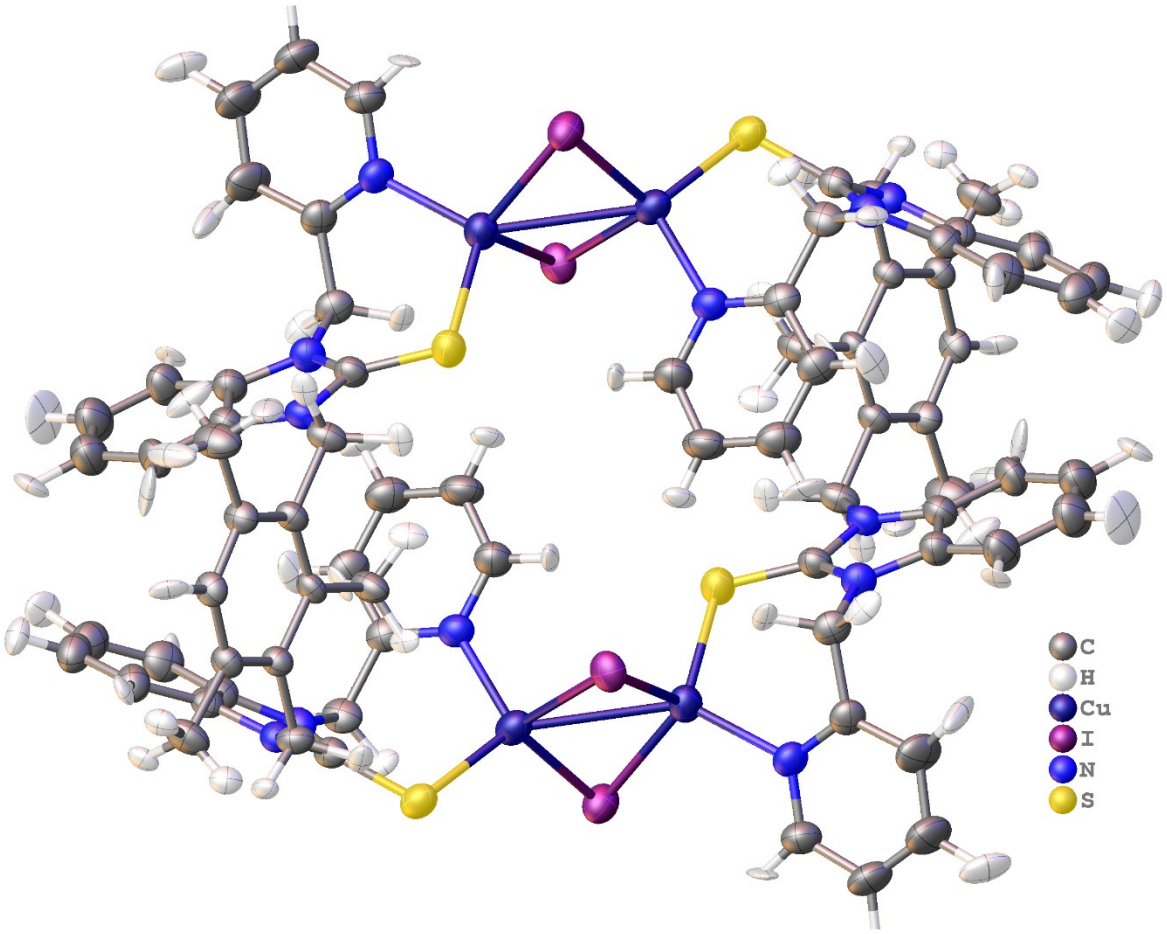

Figure S12. HAR-refined molecular structure of **2** with the PBE/def2-TZVPP model at full resolution 120 K.

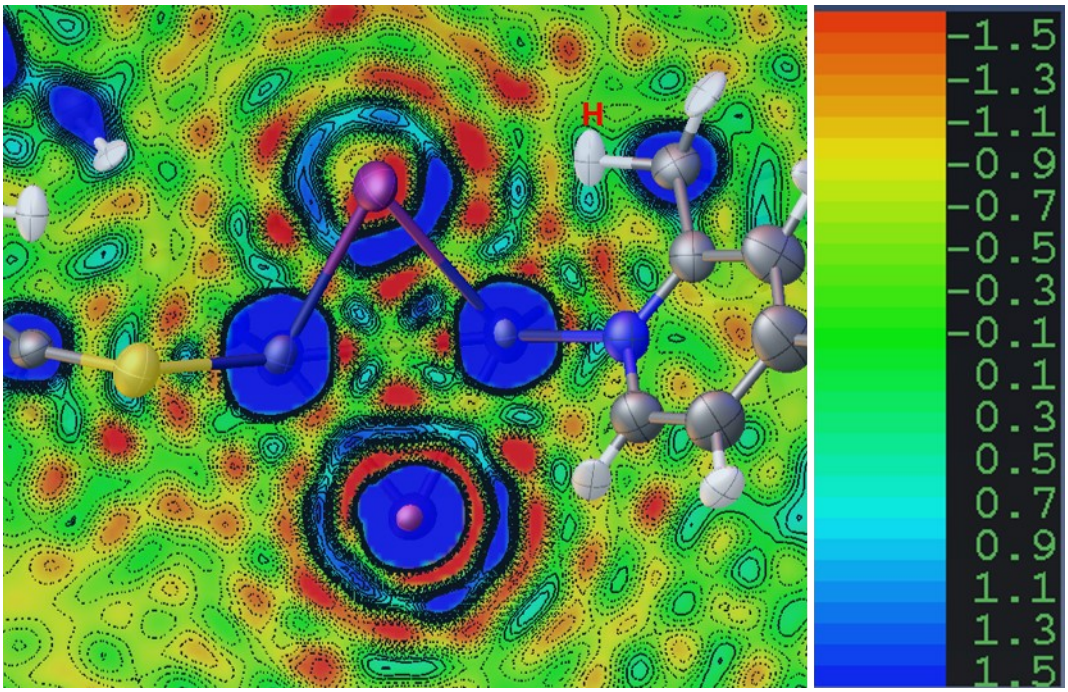

Figure S13. Fourier difference electron density maps showing the electron density (contours in the red to blue region (in eÅ^{-3}) associated with the H-atom and Cu-atom in Cu···H-C interaction at 120 K.

Table S1: The structural parameters of **1** and **2**.

	1	**2**
Empirical formula	$C_{37}H_{34}Br_2Cu_2N_6S_2$	$C_{74}H_{68}Cu_4I_4N_{12}S_4$
Formula weight	912.29	2015.40
Temperature/K	297	223
Crystal system	triclinic	Triclinic
Space Group	Pī	Pī
a/Å	10.3032(7)	10.1474(12)
b/Å	14.4037(10)	14.6541(16)
c/Å	15.4154(10)	15.5293(18)
α/°	73.897(2)	108.219(4)
β/°	77.002(2)	99.996(4)
γ/°	89.100(2)	90.325(4)
Volume/Å^3	2139.0(3)	2155.7(4)
Z	2	1
ρ_{calc}g/cm^3	1.416	1.552
μ/mm^{-1}	2.977	2.547
F(000)	915.0	988.0
Crystal size/mm^3	0.24 × 0.19 × 0.17	0.312 × 0.095 × 0.056
Radiation	MoKα (λ = 0.71073	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.462 to 54.392	4.084 to 54.562
Index ranges	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19
Reflections collected	52970	49382
Independent reflections	9496 [R_{int} = 0.1104, R_{sigma} = 0.0800]	9602 [R_{int} = 0.0598, R_{sigma} = 0.0459]
Data/restraints/parameters	9496/0/447	9602/0/439
Goodness-of-fit on F^2	1.019	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.1082	R_1 = 0.0357, wR_2 = 0.0791
Final R indexes [all data]	R_1 = 0.0769, wR_2 = 0.1212	R_1 = 0.0562, wR_2 = 0.0854
Largest diff. peak/hole / e Å^{-3}	0.69/-0.76	1.34/-0.81

Table S2: The structural parameters of **1** and **2** at 120K.

	1	**2**	**2**[a]
Empirical formula	$C_{37}H_{34}Br_2Cu_2N_6S_2$	$C_{37}H_{34}Cu_2I_2N_6S_2$	$C_{74}H_{68}Cu_4I_4N_{12}S_4$
Formula weight	912.29	1007.755	2015.40
Temperature/K	120	120.00	120
Crystal system	triclinic	triclinic	Triclinic
Space Group	Pī	Pī	Pī
a/Å	10.2301(10)	10.2882(14)	10.2882(14)
b/Å	14.3455(16)	14.6183(17)	14.6183(17)
c/Å	15.4107(18)	15.560(2)	15.560(2)
α/°	73.904(4)	72.964(4)	72.964(4)
β/°	77.156(4)	78.573(5)	78.573(5)
γ/°	88.719(4)	89.436(4)	89.436(4)
Volume/Å^3	2116.7(4)	2190.3(5)	2190.3 (5)
Z	2	2	1
ρ_{calc}g/cm^3	1.434	1.528	1.558
μ/mm^{-1}	3.022	2.506	2.506
F(000)	917.6	988.8	988.8
Crystal size/mm^3	0.12 × 0.1 × 0.08	0.12 × 0.09 × 0.08	0.12 × 0.09 × 0.08
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.08 to 53	4.04 to 54.32	4.04 to 54.32
Index ranges	-10 ≤ h ≤ 13, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19	-13 ≤ h ≤ 13, -18 ≤ k ≤ 17, -19 ≤ l ≤ 19	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19
Reflections collected	49046	60706	60706
Independent reflections	8741 [R_{int} = 0.1001, R_{sigma} = 0.0812]	9699 [R_{int} = 0.0820, R_{sigma} = 0.0541]	9699 [R_{int} = 0.0820, R_{sigma} = 0.0541]
Data/restraints/parameters	8741/0/446	9699/0/433	9699/78/736
Goodness-of-fit on F^2	1.006	1.016	1.020

Final R indexes [I>=2σ (I)]	R_1 = 0.0464, wR_2 = 0.0972	R_1 = 0.0379, wR_2 = 0.0804	R_1 = 0.0348, wR_2 = 0.0636
Final R indexes [all data]	R_1 = 0.0915, wR_2 = 0.1214	R1 = 0.0612, wR2 = 0.0894	R_1 = 0.0584, wR_2 = 0.0710
Largest diff. peak/hole / e Å^{-3}	1.01/-1.22	1.70/-1.21	1.68/-1.20

[a]Hirshfield atom refinement using NoSpher A2 with PBE/def2-TZVPP model.

Table S3: Selective bond lengths and bond angles of **2** at 120K (H atoms anisotropic refinement using NoSpherA2 in Olex2).

2(X=I) *Bond length [Å]*	
Cu(1) – S(1)	2.3173(10)
Cu(1)- Cu(2)	2.8959(7)
Cu(1)- X(1)	2.6723(6)
Cu(1)-N(3)	2.059(3)
C(1)-S(1)	1.675(4)
Cu(2)···H(23A)	2.490
Cu(1)···H(6B)	2.719
2(X=I) *Bond angle [˚]*	
C(1)-S(1)-Cu(2)	108.63(11)
S(1)-Cu(1)-X(1)	118.29(3)
N(3)-Cu(1)-X(1)	109.74(8)
X(1)-Cu(1)-X(2)	110.512(17)
Cu(1)-X(1)-Cu(2)	67.040(15)

Computational Methods

Details of Topology Analysis

The bond path represents the maximal gradient path connecting the bond critical point (BCP) with two associated local maxima of charge density. The BCP is characterized by a minimum charge density along the bond direction and a maximum charge density perpendicular to it. The BCP can be described by the number of zero eigenvalues of the associated Hessian matrix and the algebraic sum of their signs. A bond critical point is denoted as (3, -1), indicating one positive curvature of charge density along the bond path and two negative curvatures perpendicular to the bond path. The characteristics of this BCP are discussed in the main manuscript using the parameters $\rho(r)$ and $\nabla^2\rho(r)$. In addition to bond critical points, there are other types of non-degenerate critical points: (3, -3), (3, +1), and (3, +3). The (3, -3) point corresponds to the positions of nuclei (local maxima of charge density), the (3, +1) point denotes a ring critical point, and the (3, +3) point represents a cage critical point.

Another criterion mentioned in the main manuscript is mutual penetration. This parameter is derived from each interacting atom's non-bonded radius (NBR), specifically the NBR of H and Ag atoms, and the distance between them. NBR is the shortest distance between the nucleus and the $\rho(r) = 0.001$ a.u. Isosurface. Mutual penetration is calculated as the difference between the sum of the NBRs of the interacting atoms and the intermolecular distance. The mutual penetration is given by $\Delta rH = [(\text{NBR Cu} + \text{NBR of H}) - d_{Cu\cdots H}]/0.529$ a.u., where all distances are measured in Å.

Table S3: Optimized Cartesian Co-ordinates of **2** (Cartesian coordinates of the optimized structures (in Å).

I	-0.458142152	-2.861401162	-1.916390097
I	0.318863116	5.832405421	-1.761292087
Cu	-1.684668264	-3.850879204	0.299979062
Cu	-1.075450024	4.299660368	-0.000546960
S	-3.885580446	-4.734090214	-0.567498000
S	-2.622136172	2.615651285	-1.118740041
N	-6.141540557	-3.134387046	-0.196939973
N	-4.500144297	3.121569363	0.910571104
N	-5.390939407	2.323863331	-0.975862030
N	-5.028423500	-3.536698104	1.694402162
N	-2.109504264	-2.507310096	1.847912174
N	-2.315776079	5.520849458	1.157288122
C	-6.848122573	-1.741368929	-2.202467117
C	-5.993431518	-0.613001867	-2.050110108
C	-6.457867582	-3.108606034	-1.642344080
H	-7.251990650	-3.836874067	-1.826283091
H	-5.558307534	-3.491118083	-2.140237116
C	-8.050557643	-1.628939888	-2.948078173
C	-6.380185473	0.643923234	-2.593545149
C	-2.967519330	-2.807899099	2.867830248
C	-5.024964501	-3.778608117	0.325676064
C	-7.567450565	0.752895271	-3.365108200
C	-5.891506423	3.057112393	1.111595122
C	-3.955649430	-3.940245155	2.624096229
H	-3.435717416	-4.798271233	2.185761198
H	-4.415588472	-4.256400171	3.566214298
C	-6.878854595	-2.536261987	0.842125102

C	-8.372945652	-0.388146793	-3.528091215
H	-9.279994722	-0.308483765	-4.123529256
C	-4.188086288	2.690148329	-0.375518987
C	-2.944464311	-2.092562051	4.077125333
H	-3.616989368	-2.372020053	4.883456393
C	-6.459121467	2.555501374	-0.085847966
C	-4.666263402	-0.755548910	-1.321206056
H	-4.788863409	-0.646413897	-0.234414976
H	-3.938240335	-0.003560874	-1.633220075
H	-4.204660394	-1.731230993	-1.499226066
C	-8.087987672	-1.826494905	0.850571104
H	-8.632265735	-1.621689874	-0.064054964
C	-6.164806575	-2.783116019	2.042195188
C	-8.999097754	-2.799662952	-3.170146188
H	-8.523767730	-3.614519021	-3.732332228
H	-9.874454822	-2.475794908	-3.742765228
H	-9.364031826	-3.227142976	-2.225883120
C	-3.269695161	5.022151469	1.996766183
C	-5.509297413	1.882011303	-2.389732129
H	-4.483732330	1.716731261	-2.733434155
H	-5.901935396	2.725722370	-2.964029173
C	-3.521282218	3.521645371	1.940170179
H	-2.576966163	3.008955311	1.731960168
H	-3.895627252	3.166330355	2.906322252
C	-2.054620031	6.854428567	1.165541123
H	-1.289234966	7.189428564	0.471809075
C	-8.564805690	-1.371701858	2.095099191
H	-9.496701749	-0.814123799	2.134219196
C	-2.039849223	-1.024760993	4.233221344

H	-2.002825205	-0.464658954	5.163828412
C	-1.254094178	-1.460936044	1.990649186
H	-0.607015121	-1.250558046	1.145690123
C	-6.636172586	-2.328375974	3.280724278
H	-6.093550530	-2.513394999	4.201857342
C	-6.685259438	3.383173438	2.219273199
H	-6.254975415	3.757712453	3.141847266
C	-1.190513150	-0.691746993	3.164976270
H	-0.493532082	0.138083053	3.218517270
C	-8.000047568	2.048139372	-4.040143252
H	-8.134129547	2.873914437	-3.328084197
H	-8.953371654	1.905328387	-4.559683289
H	-7.268247504	2.383111381	-4.787277306
C	-7.845970574	2.382343391	-0.208162975
H	-8.292190611	1.984009376	-1.110237041
C	-2.721701057	7.746128639	2.021417186
H	-2.473088013	8.802338699	1.996688183
C	-7.852507660	-1.618765894	3.291014278
H	-8.248543648	-1.253940859	4.234943345
C	-3.966533193	5.860133568	2.887319248
H	-4.705124253	5.439199525	3.562426299
C	-8.646274592	2.721282435	0.899394103
H	-9.724181660	2.600507454	0.830334101
C	-8.076698575	3.209329457	2.096973193
H	-8.721140578	3.456859492	2.936309250
C	-3.691822138	7.239505665	2.903124248
H	-4.219193162	7.898475700	3.587620301
I	0.458137053	2.861551226	1.916468177
I	-0.318798215	-5.832437383	1.761237169

Cu	1.684672164	3.850894264	-0.299950981
Cu	1.075462920	-4.299590305	0.000547041
S	3.885635343	4.734071275	0.567430081
S	2.622164076	-2.615605220	1.118775120
N	6.141547489	3.134297108	0.196896055
N	4.500149197	-3.121464305	-0.910573025
N	5.390970258	-2.323838269	0.975881112
N	5.028386400	3.536530164	-1.694438082
N	2.109440164	2.507218157	-1.847807090
N	2.315782985	-5.520718434	-1.157362043
C	6.848169511	1.741356990	2.202455200
C	5.993479408	0.612986929	2.050115188
C	6.457912509	3.108577098	1.642295157
H	7.252046584	3.836845127	1.826185172
H	5.558367437	3.491118146	2.140190194
C	8.050607544	1.628938951	2.948065251
C	6.380234369	-0.643928171	2.593568226
C	2.967432233	2.807717162	-2.867769165
C	5.024963406	3.778501181	-0.325722983
C	7.567499461	-0.752890207	3.365134283
C	5.891511292	-3.057030334	-1.111601038
C	3.955601333	3.940051216	-2.624129149
H	3.435702313	4.798119291	-2.185836119
H	4.415525373	4.256135227	-3.566278217
C	6.878819511	2.536098042	-0.842158022
C	8.372993543	0.388154854	3.528099296
H	9.280042613	0.308502826	4.123540337
C	4.188105184	-2.690080266	0.375533067
C	2.944326211	2.092300108	-4.077015253

H	3.616836267	2.371687111	-4.883384309
C	6.459142370	-2.555466311	0.085854047
C	4.666319304	0.755511973	1.321195134
H	4.788924312	0.646321957	0.234409058
H	3.938293231	0.003539934	1.633240157
H	4.204719297	1.731203053	1.499165147
C	8.087937559	1.826307963	-0.850599023
H	8.632236630	1.621537936	0.064023045
C	6.164745455	2.782907078	-2.042222107
C	8.999148661	2.799665011	3.170114269
H	8.523815673	3.614535081	3.732275310
H	9.874498744	2.475808968	3.742749310
H	9.364092682	3.227122036	2.225844199
C	3.269676063	-5.021984413	-1.996848105
C	5.509342287	-1.882014240	2.389758212
H	4.483781231	-1.716734204	2.733470239
H	5.901984292	-2.725734308	2.964039254
C	3.521275116	-3.521484311	-1.940181101
H	2.576966063	-3.008796251	-1.731936085
H	3.895614155	-3.166125293	-2.906319166
C	2.054623931	-6.854297490	-1.165670046
H	1.289260869	-7.189328496	-0.471927993
C	8.564717582	1.371446922	-2.095117109
H	9.496604645	0.813853855	-2.134234114
C	2.039683120	1.024509057	-4.233013267
H	2.002617106	0.464348015	-5.163583328
C	1.254002075	1.460851106	-1.990447103
H	0.606943026	1.250545108	-1.145455041
C	6.636071460	2.328097034	-3.280740196

H	6.093430460	2.513083060	-4.201869259
C	6.685252347	-3.383067375	-2.219295118
H	6.254956312	-3.757572390	-3.141877185
C	1.190370056	0.691583048	-3.164720185
H	0.493368982	-0.138234992	-3.218187191
C	8.000097470	-2.048123312	4.040187332
H	8.134201462	-2.873902377	3.328135279
H	8.953412559	-1.905299325	4.559742371
H	7.268289415	-2.383097321	4.787311385
C	7.845994440	-2.382332331	0.208166055
H	8.292226489	-1.984033316	1.110250122
C	2.721671957	-7.745957609	-2.021612103
H	2.473056913	-8.802168674	-1.996924106
C	7.852393569	1.618465957	-3.291027195
H	8.248400559	1.253587919	-4.234948267
C	3.966477095	-5.859923485	-2.887469169
H	4.705043156	-5.438958485	-3.562584216
C	8.646286498	-2.721249377	-0.899407025
H	9.724195577	-2.600495394	-0.830349019
C	8.076695453	-3.209251398	-2.096997112
H	8.721127507	-3.456766430	-2.936345170
C	3.691760039	-7.239294576	-2.903332167
H	4.219103059	-7.898232649	-3.587881217