Electronic Supplementary Information

Interplay of the Cu···Cu distance and coordination geometry as a factor affecting the quantum efficiency in dimeric copper(I) halide complexes with derivatives of 4-pyrazolylpyrimidine-2-thiol

Sofia V. Skvortsova,*[a,b] Fyodor K. Verkhov,[b,c] Elena B. Nikolaenkova,[c] Marianna I. Rakhmanova,[a] Tatiana E. Kokina,[a] Taisiya S. Sukhikh,[a] Nikita A. Shekhovtsov *[a] and Mark B. Bushuev *[a]

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia. E-mail: s.skvortsova@g.nsu.ru (S. V. Skvortsova), shekhovtsov@niic.nsc.ru (Nikita A. Shekhovtsov), bushuev@niic.nsc.ru (Mark B. Bushuev)*.
[b] *Novosibirsk State University, 2, Pirogova str., Novosibirsk, 630090, Russia*.
[c] *N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences, 9, Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia*.

Table of contents

Experimental section

General Information

All solvents were of analytical grade. 2-Benzylthio-4-chloropyrimidine and 2-benzylthio-4-chloro-6-methylpyrimidine were synthesized according to literature procedures.[1,2] All other reactants were purchased from commercial suppliers and used as received. Elemental analyses were performed with a EuroEA3000 analyser using standard technique. ^{1}H and ^{13}C NMR spectra were registered on Bruker AV-300 (300.13 and 75.46 MHz), Bruker AV-400 (400.13 and 100.61 MHz) and Bruker DRX-500 (500.13 and 125.76 MHz) spectrometers using the residual signals of the solvents: $CDCl_3$ at 7.24 ppm for ^{1}H and 76.9 ppm for ^{13}C and DMSO-d_6 at 2.50 ppm for ^{1}H and 39.5 ppm for ^{13}C with respect to TMS as the internal standard. IR spectra were recorded in KBr on a Bruker Vector-22 spectrometer. Melting points were determined on a Mettler Toledo FP-900 instrument. High-resolution mass spectra were recorded on a DFS Thermo Electron instrument (ionizing electron energy 70 eV, direct sample injection into the ion source). Corrected photoluminescence spectra were recorded on a Fluorolog 3 spectrometer (Horiba Jobin Yvon) with a cooled PC177CE-010 photon detection module equipped with R2658 photomultiplier. Luminescence decay kinetics were recorded using a Xe-flash lamp and a NanoLED pulsed light source with a NanoLED-C2 controller. Diffuse reflectance spectra were recorded on a UV-3101 PC Shimadzu spectrophotometer. $BaSO_4$ was used for the baseline. Spectra are reported as the Kubelka-Munk function, $F(R) = (1 – R)^2/(2R)$, where R is the diffuse reflectance of the compounds relative to $BaSO_4$. X-ray powder diffraction patterns of the compounds were recorded on a Tongda TD-3700 diffractometer with Dectris Mythen2 1D detector (energy-discriminating Cu-Kα radiation).

Synthesis of 2-benzylthio-4-hydrazinylpyrimidine

Hydrazine hydrate (0.27 ml, 5.34 mmol) was added to a solution of 2-benzylthio-4-chloropyrimidine (0.42 g, 1.78 mmol) in EtOH (6 ml). The reaction mixture was heated under reflux for 3.5 h. After cooling down to room temperature, the resulting mixture was diluted with water, the precipitate formed was filtered off, washed with H_2O and dried. Yield: 0.25 g (60%), m. p. 136.6–138.4°C. ^{1}H NMR (DMSO-d_6, 300.13 MHz) δ (ppm): 8.51 (s, 1H, NH), 7.95 (br. s, 1H, 6-$H_{pyrimidine}$), 7.42–7.39 (m, 2H, 2’, 6’-H_{Ph}), 7.31–7.19 (m, 3H, 3’, 5’, 4’-H_{Ph}), 6.47 (br. s, 1H, 5-$H_{pyrimidine}$), 4.38 (s, 2H, NH_2), 4.31 (s, 2H, CH_2). ^{13}C NMR (DMSO-d_6, 125.76 MHz) δ (ppm): 168.78 (br.), 164.86 (br.), 155.13 (br.), 138.67, 128.86 (2), 128.28 (2), 126.78, 98.44 (br.), 33.80. IR (KBr, ν cm^{-1}): 1660s, 1574s, 1558s, 1518m, 1496m, 1452w, 1402vs, 1369m, 1331s, 1228s, 1211m, 1196m, 1144m, 1072w, 976m, 897w, 823m, 768m, 729m, 698s, 604w, 565w. High-resolution mass spectrum, m/z: Calc. for $C_{11}H_{12}N_4S$ 232.0777. Found 232.0780.

Synthesis of 2-benzylthio-4-hydrazinyl-6-methylpyrimidine

A mixture of 2-benzylthio-4-chloro-6-methylpyrimidine (2.1 g, 8.38 mmol), hydrazine hydrate (1.25 ml, 25 mmol) and EtOH (25 ml) was heated under reflux for 3 h. After cooling, the solvent was removed by distillation under reduced pressure, and the residue was treated with water. The precipitate formed was filtered off, washed with H_2O and dried. Yield: 1.67 g (81%), m. p. 92.3–93.5°C. ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ (ppm): 7.40–7.39 (m, 2H, 2’,6’-H_{Ph}), 7.28–7.25 (m, 2H, 3’,5’-H_{Ph}), 7.22–7.18 (m, 1H, 4’-H_{Ph}), 6.31 (br. s, 1H, NH), 6.19 (s, 1H, 5-$H_{pyrimidine}$), 4.35 (s, 2H, CH_2), 3.75 (br. s, 2H, NH_2), 2.29 (s, 3H, Me). ^{13}C NMR (DMSO-d_6, 125.76 MHz) δ (ppm): 168.14 (br.), 165.71 (br.), 164.73 (br.), 138.99, 129.04 (2), 128.33 (2), 126.82, 96.42 (br.), 33.76, 23.61. IR (KBr, ν cm^{-1}): 1653s, 1587vs, 1568s, 1512w, 1495m, 1412vs, 1360m, 1282s, 1234s, 1192m, 1128m, 1030w, 987m, 972m, 924m, 885m, 864w, 837w, 766m, 723m, 696s. High-resolution mass spectrum, m/z: Calc. for $C_{12}H_{14}N_4S$ 246.0934. Found 246.0931.

Synthesis of 2-benzylthio-4-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyrimidine (L^H)

A mixture of 2-bezylthio-4-hydrazinylpyrimidine (0.232 g, 1 mmol) and acetylacetone (0.12 ml, 1.2 mmol) in EtOH (7 ml) was refluxed for 2 h. The reaction mixture was cooled, the solvent was removed by distillation under reduced pressure, and the residue was purified by column chromatography (SiO_2, $CHCl_3$) to give the title ligand. Yield: 0.228 g (77%), m. p. 69.2–69.9°C. Anal. Calc. for $C_{16}H_{16}N_4S$: C, 64.83; H, 5.44; N, 18.90; S, 10.82. Found: C, 65.14; H, 5.61; N, 18.63; S, 10.56%. ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ (ppm):

8.46 (d, 1H, *J* = 5.6 Hz, 6-$H_{pyrimidine}$), 7.57 (d, 1H, *J* = 5.6 Hz, 5-$H_{pyrimidine}$), 7.41–7.39 (m, 2H, 2', 6'-H_{Ph}), 7.32–7.28 (m, 2H, 3', 5'-H_{Ph}), 7.26–7.22 (m, 1H, 4'-H_{Ph}), 5.99 (s, 1H, $H_{pyrazole}$), 4.43 (s, 2H, CH_2), 2.65 (br. s, 3H, Me), 2.26 (s, 3H, Me). ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ (ppm): 171.00, 158.95, 158.08, 151.86, 142.79, 136.61, 128.76 (2), 128.45 (2), 127.18, 110.92, 105.89, 35.21, 15.53, 13.60. IR (KBr, ν cm^{-1}): 1581s, 1560vs, 1549vs, 1479m, 1466m, 1441s, 1412m, 1383m, 1344vs, 1275w, 1213m, 1163m, 1142m, 1065w, 1026w, 970m, 829m, 810w, 733w, 714m, 698w, 683m.

Synthesis of 2-benzylthio-4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine (L^{Me})

2-Benzylthio-4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine was obtained similarly from 2-benzylthio-4-hydrazinyl-6-methylpyrimidine (0.492 g, 2 mmol), acetylacetone (0.24 ml, 2.4 mmol) and EtOH (15 ml). Yield: 0.59 g (95%), m. p. 49–51°C. Anal. Calc. for $C_{17}H_{18}N_4S$: C, 65.77; H, 5.85; N, 18.05; S, 10.33. Found: C, 65.84; H, 5.88; N, 18.10; S, 10.28%. ^{1}H NMR ($CDCl_3$, 300.13 MHz) δ (ppm): 7.44 (s, 1H, 5-$H_{pyrimidine}$), 7.41–7.39 (m, 2H, 2', 6'-H_{Ph}), 7.32–7.27 (m, 2H, 3', 5'-H_{Ph}), 7.25–7.20 (m, 1H, 4'-H_{Ph}), 5.97 (s, 1H, $H_{pyrazole}$), 4.42 (s, 2H, CH_2), 2.63 (s, 3H, Me), 2.47 (s, 3H, Me), 2.26 (s, 3H, Me). ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ (ppm): 170.49, 168.77, 159.07, 151.56, 142.74, 136.87, 128.75 (2), 128.40 (2), 127.09, 110.62, 104.90, 35.14, 24.09, 15.49, 13.59. IR (KBr, ν cm^{-1}): 1585s, 1564vs, 1481m, 1468m, 1441s, 1396s, 1363s, 1288s, 1242w, 1194m, 1134m, 1070w, 1030w, 968m, 920w, 847m, 835w, 808w, 787w, 737m, 714m, 696w.

Synthesis of $[Cu_2(L^H)_2I_2]$ (form I)

A solution of CuI (19.0 mg, 0.1 mmol) in MeCN (2 ml) was added to a solution of L (29.6 mg, 0.1 mmol) in MeCN (2 ml). The resulting yellow-orange solution was allowed to slowly evaporate at room temperature for 3 days, yielding orange crystals of the complex. The obtained crystals were filtered off, washed with MeCN, and dried in air. Yield: 31.6 mg (65%). Anal. Calcd for $C_{32}H_{32}Cu_2I_2N_8S_2$: C, 39.5; H, 3.3; N, 11.5; S, 6.6. Found: C, 39.3; H, 3.3; N, 11.5; S, 7.0%. Single crystals of the complex were obtained by slow crystallization at room temperature from the supernatant.

Synthesis of $[Cu_2(L^H)_2I_2]$ (form II)

A solution of CuI (19.0 mg, 0.1 mmol) in MeCN (2 mL) was added to a solution of L (29.6 mg, 0.1 mmol) in MeCN (2 mL). The resulting yellow-orange solution was stirred for 10 minutes and then quickly concentrated to ca. 1 mL, which yielded a yellow precipitate of the complex. The obtained precipitate was filtered off, washed with MeCN, and dried in air. Yield: 39.3 mg (81%). Anal. Calcd for $C_{32}H_{32}Cu_2I_2N_8S_2$: C, 39.5; H, 3.3; N, 11.5; S, 6.6. Found: C, 39.1; H, 3.3; N, 11.4; S, 6.9%. Slow evaporation of the supernatant led to the formation of crystals of form I. Single crystals of **form II** were obtained from the supernatant that was seeded with about 1 mg of form II and left to stand at 5°C for a week. XRPD data for the sample obtained by quick precipitation are in agreement with single-crystal X-ray diffraction data for **$[Cu_2(L^H)_2I_2]$ (form II)**.

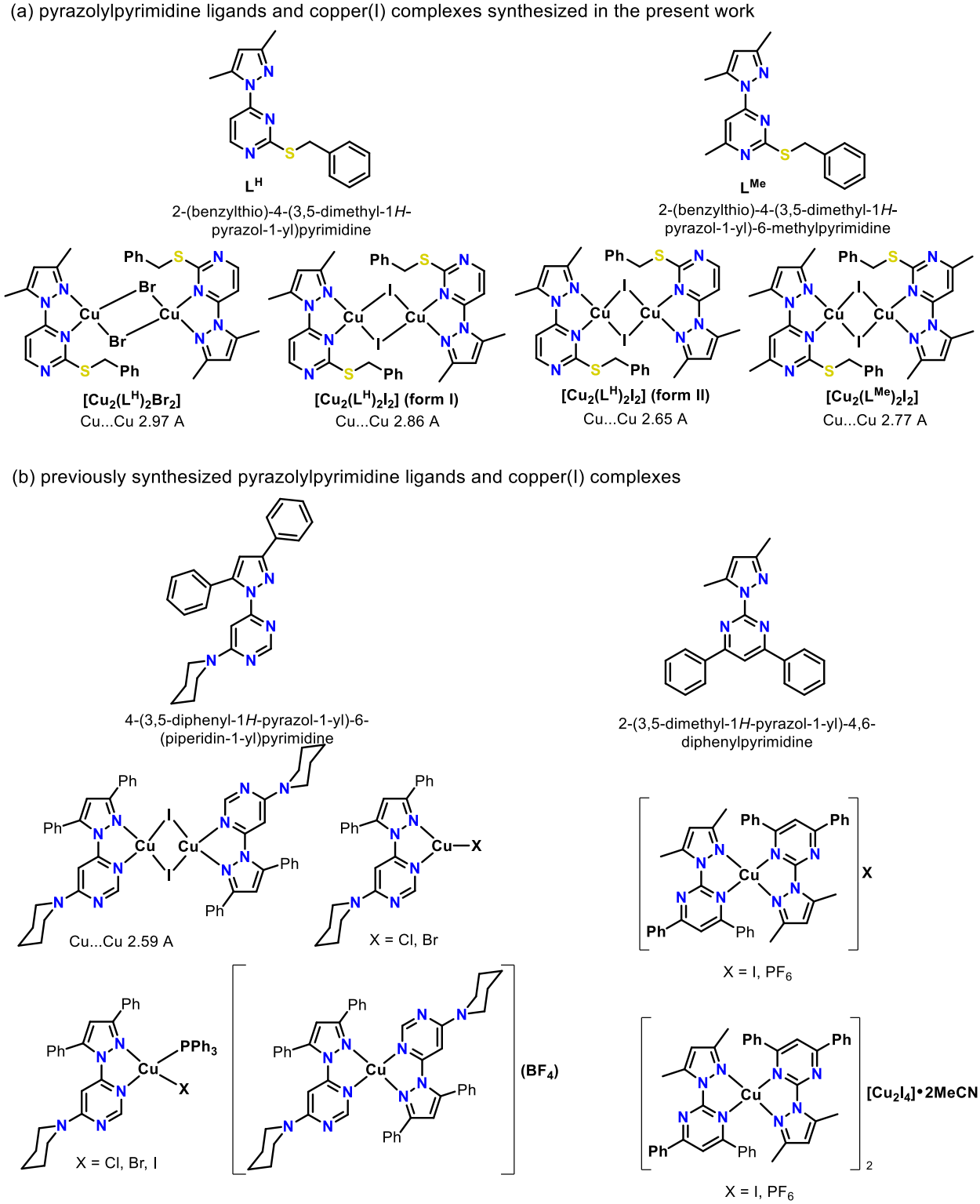
Synthesis of $[Cu_2(L^H)_2Br_2]$

The complex was synthesized by the same procedure as $[Cu_2(L^H)_2I_2]$ (form II). Orange powder was obtained. Yield: 34.3 mg (78%). Anal. Calcd for $C_{32}H_{32}Br_2Cu_2N_8S_2$: C, 43.7; H, 3.7; N, 12.7; S, 7.3. Found: C, 43.2; H, 3.8; N, 12.8; S, 7.8%. When attempting to crystallize the complex in air, oxidation occurred. Therefore, single crystals of the complex were obtained by slow crystallization from the supernatant in an argon atmosphere.

Synthesis of $[Cu_2(L^{Me})_2I_2]$

Both slow crystallization and quick precipitation (procedures for the form I and the form II of $[Cu_2(L^H)_2I_2]$, respectively) afforded the same complex, according to XRPD data. Yellow-orange powder was obtained. Yield: 39.3 mg (89%). Anal. Calcd for $C_{34}H_{36}Cu_2I_2N_8S_2$: C, 40.8; H, 3.6; N, 11.2; S, 6.4. Found: C, 40.2; H, 3.7; N, 11.3; S, 6.9%. Single crystals of the complex were obtained by slow crystallization at room temperature from the supernatant.

Structural formulae of ligands and complexes



Scheme S1. Structural formulae of pyrazolylpyrimidine ligands and copper(I) complexes synthesized in the present work and previously synthesized pyrazolylpyrimidine ligands and copper(I) complexes based on them.[3-6]

X-ray crystal structures

Single-crystal X-ray diffraction data for the crystals of **L^H**, **L^{Me}**, **$[Cu_2(L^H)_2Br_2]$**, **$[Cu_2(L^H)_2I_2]$ (form I)**, **$[Cu_2(L^H)_2I_2]$ (form II) and $[Cu_2(L^{Me})_2I_2]$** were collected at 150 K with a Bruker D8 Venture diffractometer (0.5° ω- and ϕ-scans, fixed-χ three circle goniometer, CMOS PHOTON III detector, IμS 3.0 microfocus source, focusing Montel mirrors, λ = 0.71073 Å MoK_α radiation (**L^H**, **$[Cu_2(L^H)_2Br_2]$**, **$[Cu_2(L^H)_2I_2]$ (form I),** and **$[Cu_2(L^H)_2I_2]$ (form II)**) or λ = 1.54178 Å CuK_α radiation (**L^{Me} and $[Cu_2(L^{Me})_2I_2]$**), N_2-flow thermostat). Data reduction was performed routinely via APEX 3 suite.[7] The crystal structures were solved using the ShelXT[8] and were refined using ShelXL[9] programs assisted by Olex2 GUI.[10] Atomic displacements for non-hydrogen atoms were refined in harmonic anisotropic approximation. Hydrogen atoms were located either geometrically (**$[Cu_2(L^H)_2I_2]$ (form I)**, **$[Cu_2(L^H)_2I_2]$ (form II)**), or from residual electron density map (**L^H**), or by combining both methods (**$[Cu_2(L^{Me})_2I_2]$**, **$[Cu_2(L^H)_2Br_2]$**, **L^{Me}**) and refined in a riding model or isotropically, depending on the method used. In the structure of **$[Cu_2(L^H)_2I_2]$ (form II)**, the benzylthio group is disordered over two positions with the occupancy factors of 0.58 and 0.42. The complex **$[Cu_2(L^{Me})_2I_2]$** tends to twin by non-merohedry. The data were reduced with two domains (fraction of 0.85/0.15) with the same unit cell parameters. For the final refinement, the merged data for the major domain were used. The structures of **L^H**, **L^{Me}**, **$[Cu_2(L^H)_2Br_2]$**, **$[Cu_2(L^H)_2I_2]$ (form I)**, **$[Cu_2(L^H)_2I_2]$ (form II) and $[Cu_2(L^{Me})_2I_2]$** were deposited to the Cambridge Crystallographic Data Centre (CCDC) as a supplementary publication, CCDC 2424475-2424480.

Computational details

Photophysical properties of the free ligands and the copper(I) complexes were studied by density functional theory (DFT) and time-dependent density functional dependent theory (TDDFT) methods in Gaussian 16 software package. The hybrid functional PBE0 with Stuttgart RSC 1997 basis set and its corresponding pseudopotential for the copper atom, 6-311G(d) basis set for the iodine atom and the 6-31+G(d) basis set for other atoms were adopted for all computations. The QM/MM approach, which is implemented in the two-layer ONIOM model, was adopted in order to simulate the environment of all studied molecules in the crystal structure in the S_0 state. The QM part (central molecule, ESI, Figures S41 – S45) was treated with the above-mentioned PBE0/ Stuttgart RSC 1997/6-31+G(d) level of theory, the universal force field (UFF) was adopted for the MM part (surrounding molecules, ESI, Figures S41 – S45). The first triplet excited state (T_1) of the copper(I) complexes was optimized with unrestricted DFT in the gas phase. The relaxed potential energy scans of the T_1 state along the Cu···Cu distance coordinate were also carried out by unrestricted DFT. Vertical electronic emission energies were theoretically simulated by TDDFT calculations within the Tamm–Dancoff approximation at the triplet excited state optimized geometries. The D3 version of Grimme's dispersion with Becke-Johnson damping was employed for each calculation. All frequencies in the harmonic approximation for the calculated global minimum energy geometries are positive, confirming that the optimized molecular geometries correspond to the real minima on the potential energy surfaces. The atomic coordinates of all optimized geometries are given in ESI, Tables S3 – S6. The geometries and molecular orbitals were visualized using ChemCraft software.

NMR data

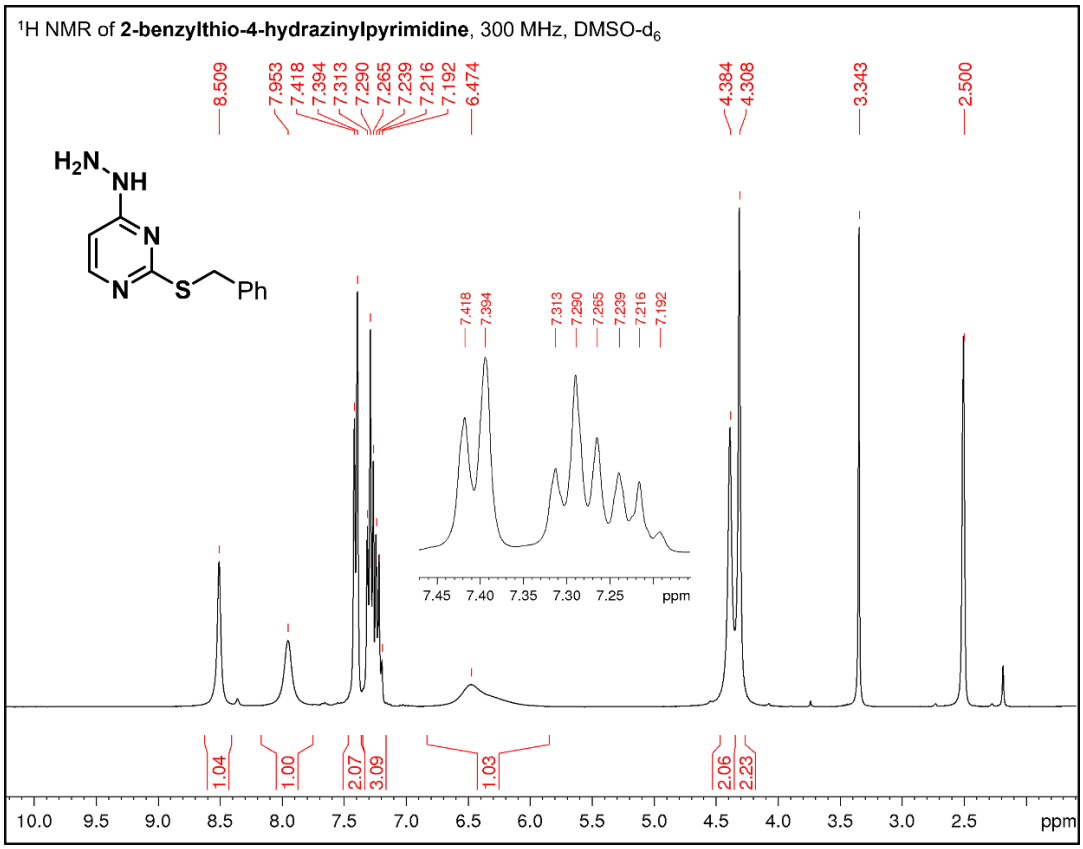


Figure S1. ^{1}H NMR spectrum of 2-benzylthio-4-hydrazinylpyrimidine.

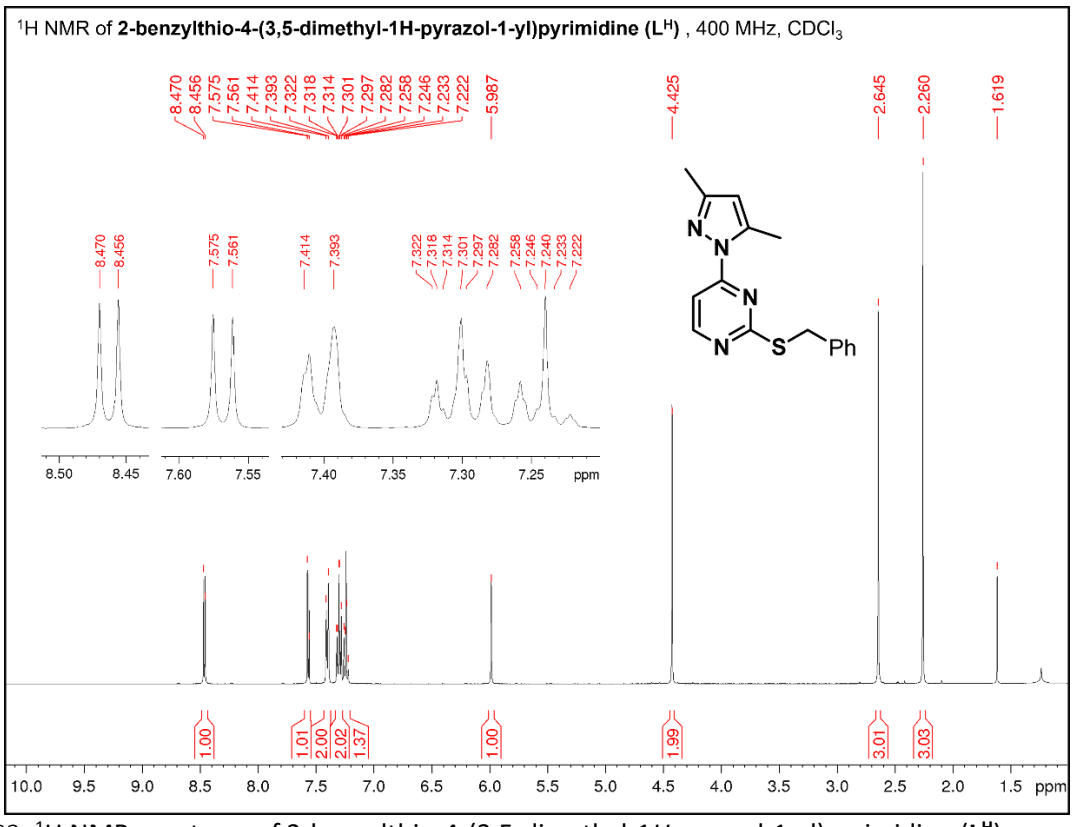


Figure S2. ^{1}H NMR spectrum of 2-benzylthio-4-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyrimidine (**L^{H}**).

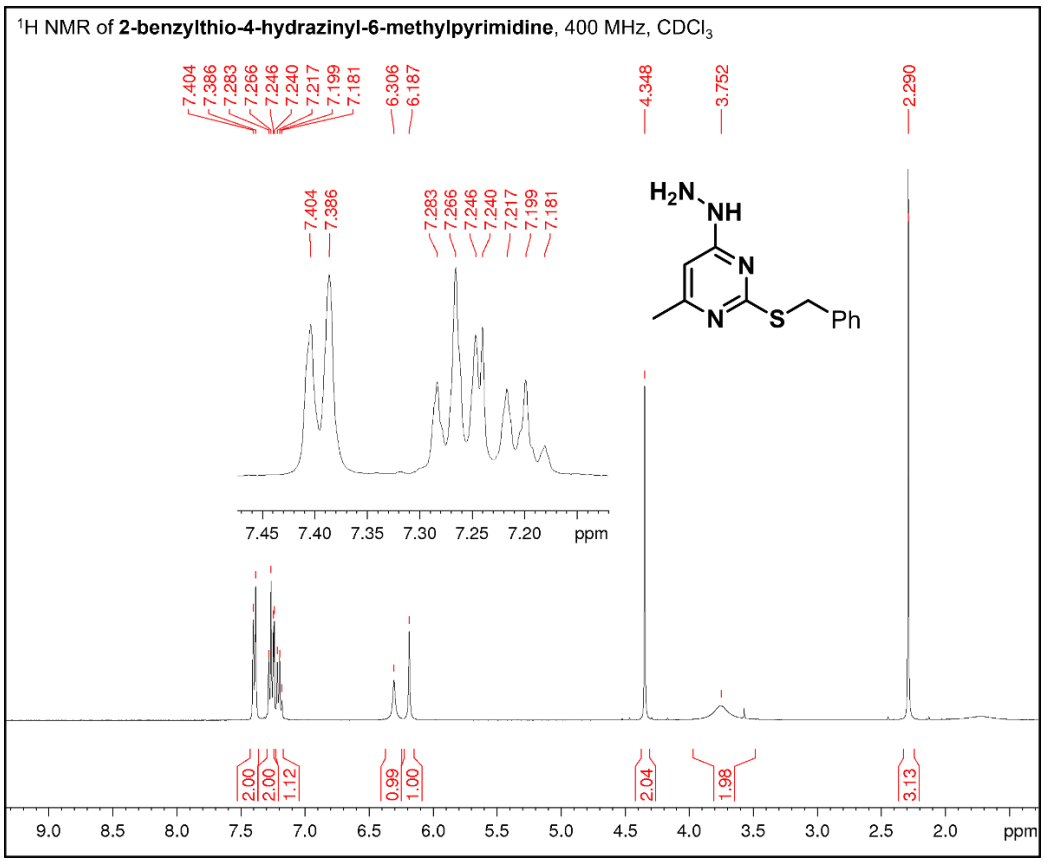


Figure S3. ^{1}H NMR spectrum of 2-benzylthio-4-hydrazinyl-6-methylpyrimidine.

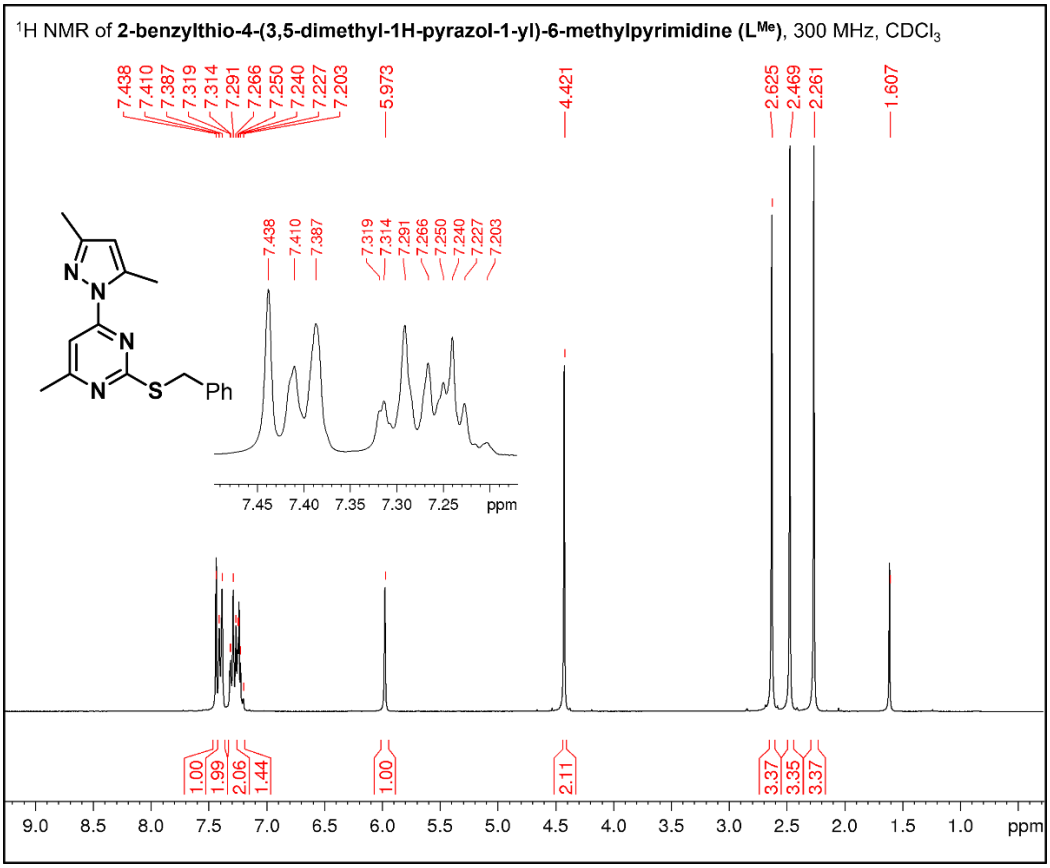


Figure S4. ^{1}H NMR spectrum of 2-benzylthio-4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine (**L^{Me}**).

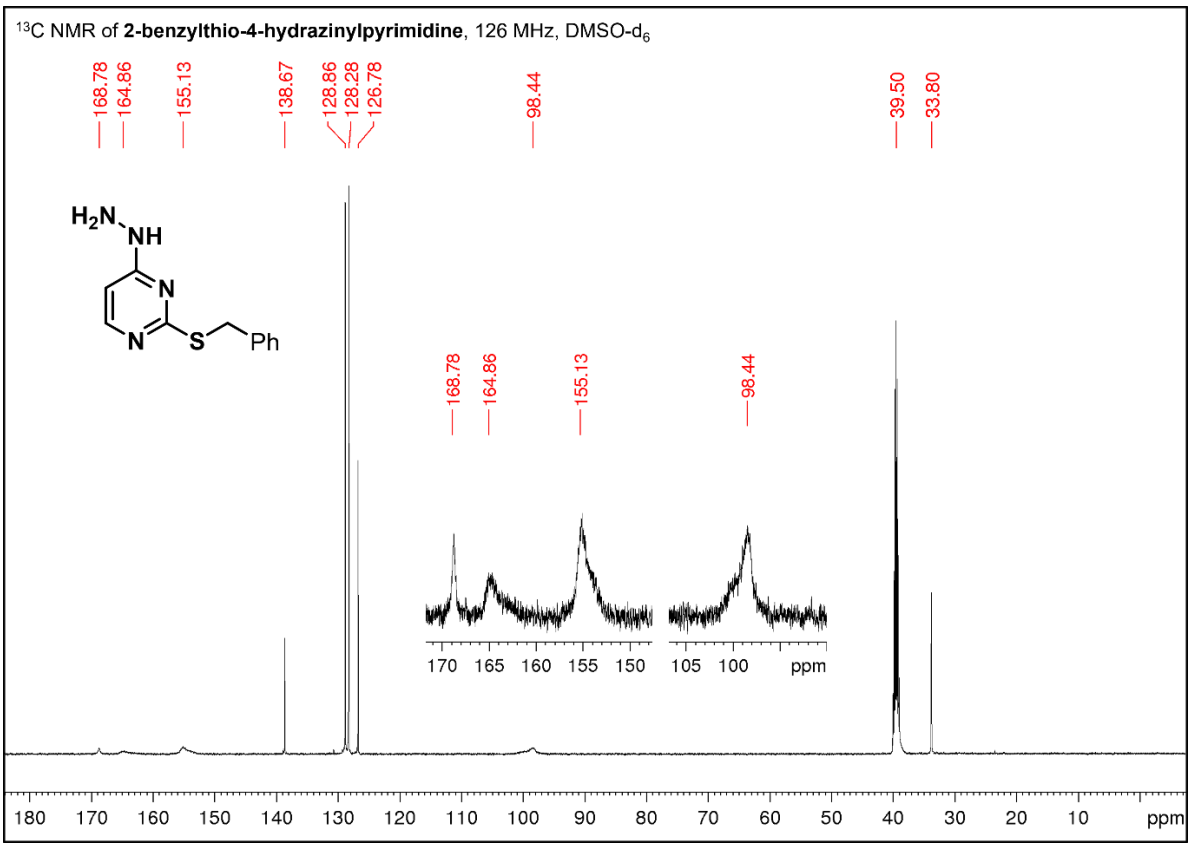


Figure S5. ^{13}C NMR spectrum of 2-benzylthio-4-hydrazinylpyrimidine.

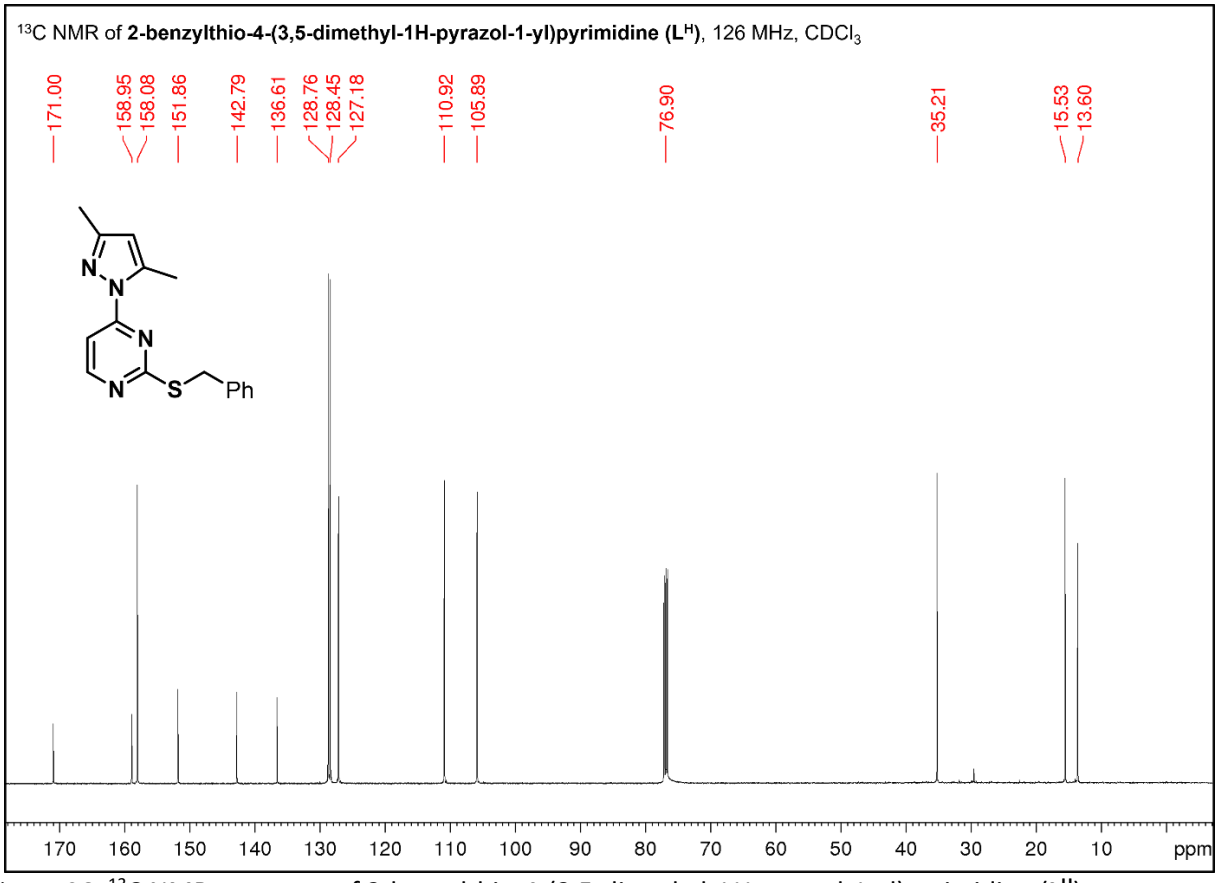


Figure S6. ^{13}C NMR spectrum of 2-benzylthio-4-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyrimidine (**L^{H}**).

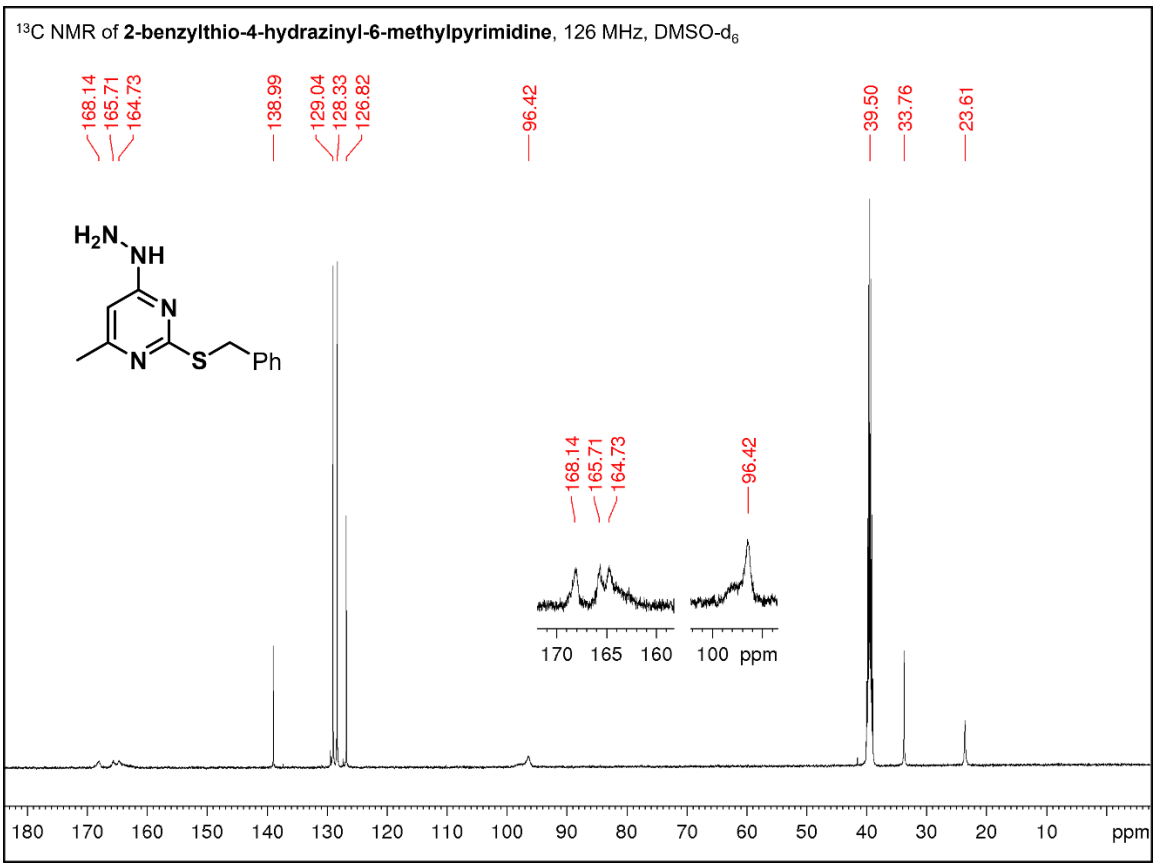


Figure S7. ^{13}C NMR spectrum of 2-benzylthio-4-hydrazinyl-6-methylpyrimidine.

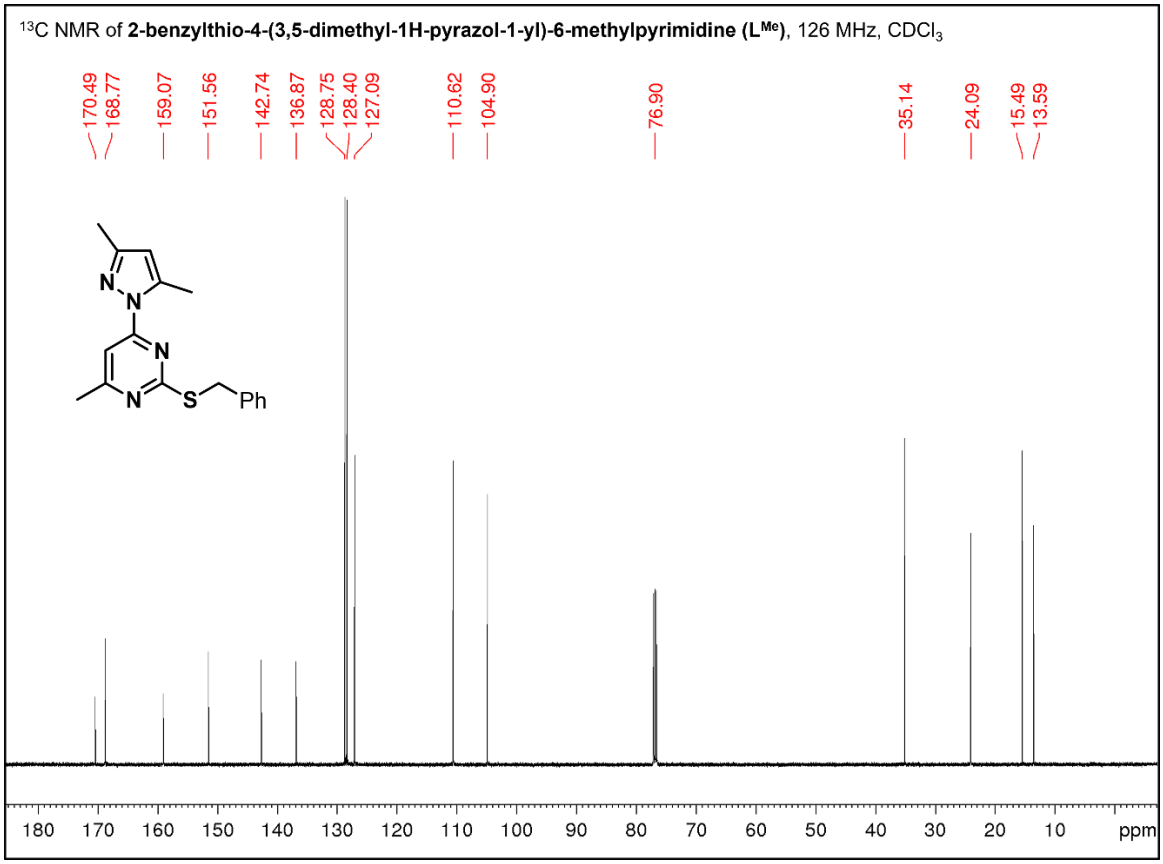


Figure S8. ^{13}C NMR spectrum of 2-benzylthio-4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine (**L^{Me}**).

Structural data

Table S1. Crystal data and structure refinement for **L^{H}** and **L^{Me}**.

Compound	**L^{H}**	**L^{Me}**
Empirical formula	$C_{16}H_{16}N_4S$	$C_{17}H_{18}N_4S$
M_r, g/mol	296.39	310.41
Crystal system	*Monoclinic*	*Monoclinic*
Space group	*$P2_1/c$*	*$P2_1/m$*
Temperature, K	150(2)	150(2)
a, Å	4.9099(1)	11.0358(8)
b, Å	24.0621(5)	6.7859(6)
c, Å	12.6078(2)	11.4683(7)
α, deg.	90	90
β, deg.	95.836(1)	100.397(5)
γ, deg.	90	90
V, Å^3	1481.80(5)	844.73(11)
Z	4	2
Density (calculated), g/cm^3	1.329	1.220
μ, mm^{-1}	0.22	1.71
F(000)	624	328
Crystal size, mm	0.18 × 0.14 × 0.08	0.09 × 0.05 × 0.03
θ range for data collection, deg.	2.4 — 27.9	3.9 – 74.6
Index ranges	−6 ≤ *h* ≤ 6, −31 ≤ *k* ≤ 31, −16 ≤ *l* ≤ 16	−13 ≤ *h* ≤ 13, −8 ≤ *k* ≤ 8, −13 ≤ *l* ≤ 14
Reflections collected / independent	27953 / 3558	8763 / 1864
R_{int}	0.0255	0.0840
Observed reflections [I > 2σ(I)]	3244	1495
Goodness-of-fit on F^2	1.050	1.032
Final R indices [I > 2σ(I)]	R_1 = 0.0302, wR_2 = 0.0799	R_1 = 0.0385, wR_2 = 0.0951
R indices (all data)	R_1 = 0.0334, wR_2 = 0.0827	R_1 = 0.0561, wR_2 = 0.1027
Largest diff. peak / hole, *e*/Å^3	0.27 / −0.19	0.18 / −0.36
CCDC Number	2424480	2424475

Table S2. Crystal data and structure refinement for **$[Cu_2(L^H)_2Br_2]$**, **$[Cu_2(L^H)_2I_2]$ (form I)**, **$[Cu_2(L^H)_2I_2]$ (form II)** and **$[Cu_2(L^{Me})_2I_2]$**.

Compound	**$[Cu_2(L^H)_2I_2]$ (form I)**	**$[Cu_2(L^H)_2I_2]$ (form II)**	**$[Cu_2(L^H)_2Br_2]$**	**$[Cu_2(L^{Me})_2I_2]$**
Empirical formula	$C_{32}H_{32}Cu_2I_2N_8S_2$	$C_{32}H_{32}Cu_2I_2N_8S_2$	$C_{32}H_{32}Br_2Cu_2N_8S_2$	$C_{34}H_{36}Cu_2I_2N_8S_2$
M_r, g/mol	973.65	973.65	879.67	1001.71
Crystal system	*Triclinic*	*Monoclinic*	*Triclinic*	*Triclinic*
Space group	*P-1*	*$P2_1/c$*	*P-1*	*P-1*
Temperature, K	150(2)	150(2)	150(2)	150(2)
a, Å	9.5514(10)	9.405(2)	9.3376(3)	9.7622(5)
b, Å	10.0363(12)	9.845(2)	9.7651(5)	9.9792(5)
c, Å	10.101(1)	19.150(5)	10.1034(4)	10.2039(5)
α, deg.	77.316(4)	90	76.831(2)	77.565(3)
β, deg.	70.532(4)	91.785(8)	72.557(1)	71.076(2)
γ, deg.	76.891(4)	90	76.000(2)	79.975(3)
V, Å^3	878.14(17)	1772.3(7)	840.70(6)	912.40(8)
Z	1	2	1	1
Density (calculated), g/cm^3	1.841	1.825	1.738	1.823
μ, mm^{-1}	3.12	3.10	3.80	16.08
F(000)	476	952	440	492
Crystal size, mm	0.1 × 0.08 × 0.03	0.2 × 0.04 × 0.02	0.17 × 0.05 × 0.02	0.1 × 0.04 × 0.04
θ range for data collection, deg.	2.8 — 30.5	2.1 — 26.4	2.3 — 28.3	4.6 — 63.7
Index ranges	−13 ≤ *h* ≤ 13, −14 ≤ *k* ≤ 14, −12 ≤ *l* ≤ 14	−11 ≤ *h* ≤ 11, −12 ≤ *k* ≤ 12, −23 ≤ *l* ≤ 22	−12 ≤ *h* ≤ 12, −13 ≤ *k* ≤ 13, −13 ≤ *l* ≤ 13	−10 ≤ *h* ≤ 11, −10 ≤ *k* ≤ 11, −11 ≤ *l* ≤ 11
Reflections collected / independent	11341 / 5350	18304 / 3619	9828 / 4178	7325 / 2861
R_{int}	0.0376	0.0682	0.0290	0.0918
Observed reflections [I > 2σ(I)]	4298	2795	3461	2672
Goodness-of-fit on F^2	1.036	1.300	1.033	1.106
Final R indices [I > 2σ(I)]	R_1 = 0.0369, wR_2 = 0.0650	R_1 = 0.0898, wR_2 = 0.2021	R_1 = 0.0318, wR_2 = 0.0644	R_1 = 0.0379, wR_2 = 0.1011
R indices (all data)	R_1 = 0.0489, wR_2 = 0.0713	R_1 = 0.1146, wR_2 = 0.2117	R_1 = 0.0417, wR_2 = 0.0684	R_1 = 0.0407, wR_2 = 0.1038
Largest diff. peak / hole, *e*/Å^3	0.71 / −0.60	1.24 / −1.73	0.53 / −0.38	0.86 / −0.83
CCDC Number	2424478	2424479	2424477	2424476

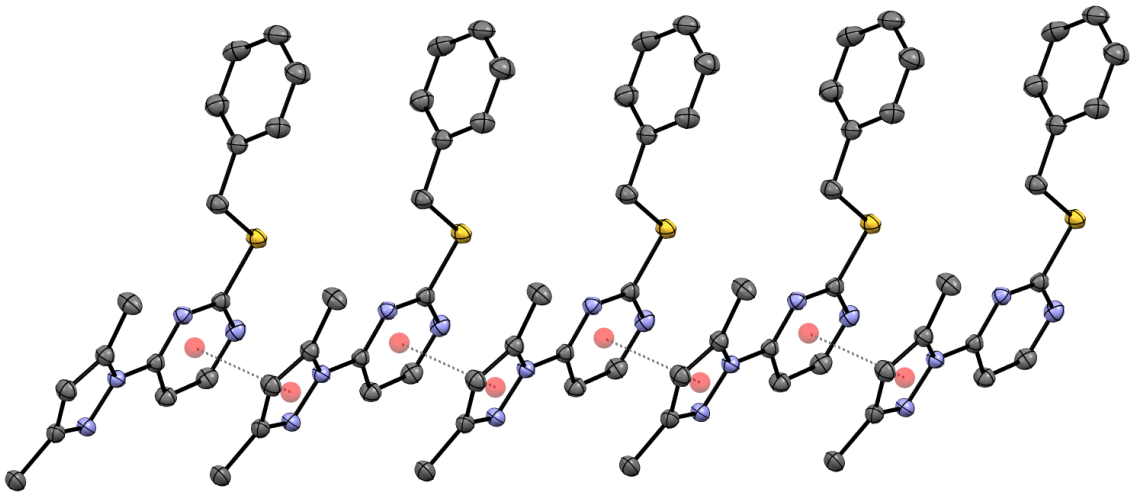


Figure S9. Supramolecular chain in the structure of $\mathbf{L^H}$ (hydrogen atoms are omitted for clarity).

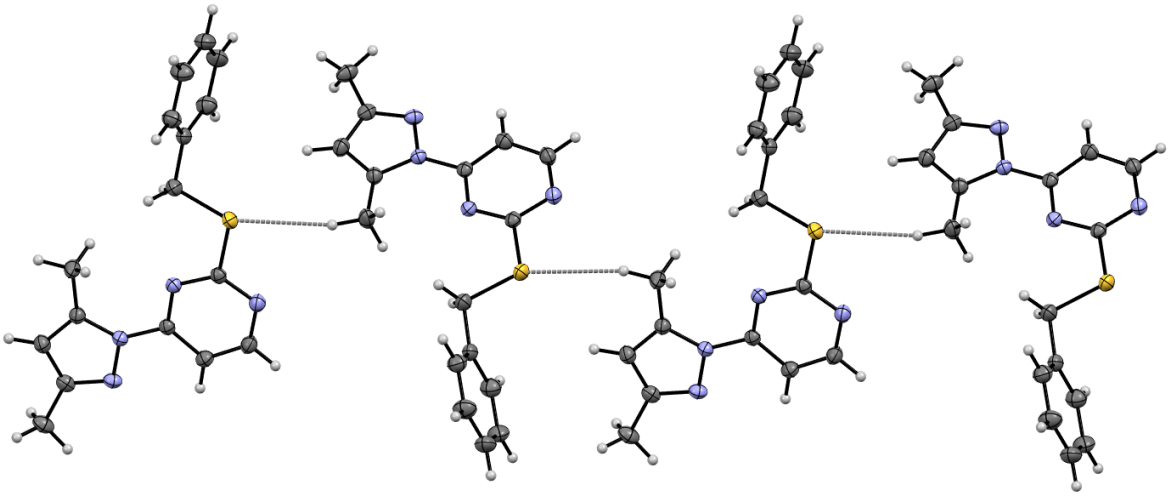


Figure S10. C–H···S interactions between supramolecular chains in the structure of $\mathbf{L^H}$.

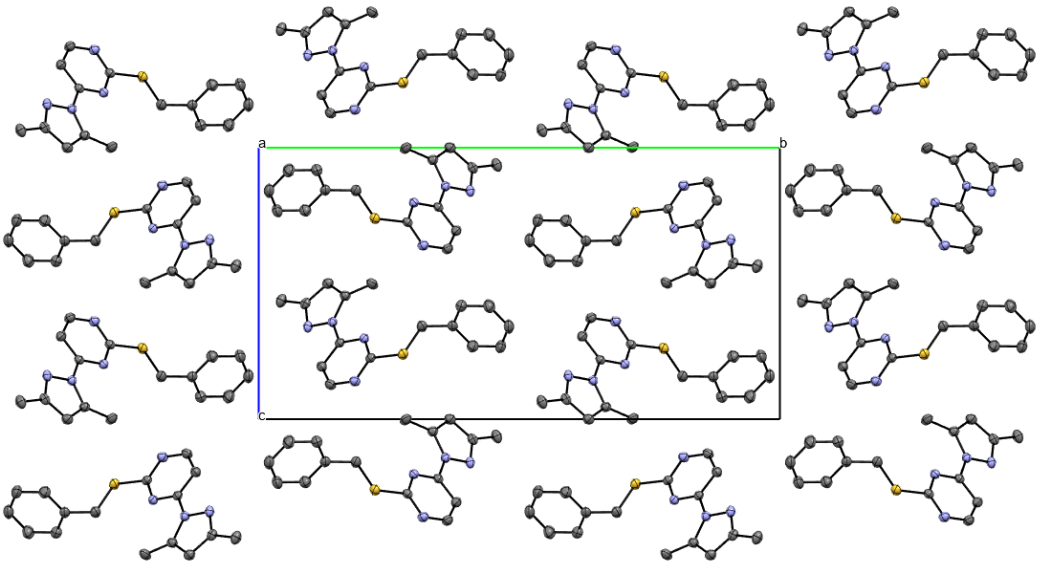


Figure S11. Packing of **L^{H}** (view along the *a* axis, hydrogen atoms are omitted for clarity).

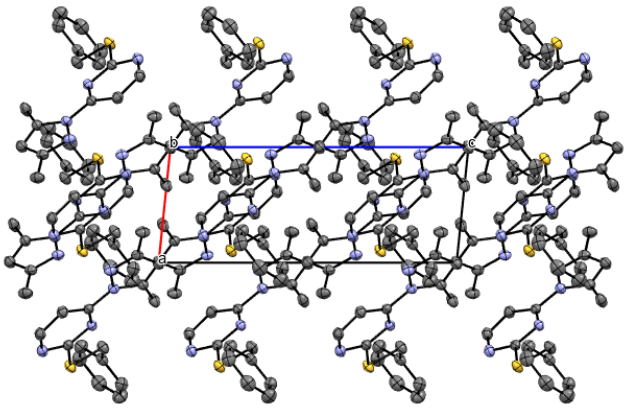


Figure S12. Packing of **L^{H}** (view along the *b* axis, hydrogen atoms are omitted for clarity).

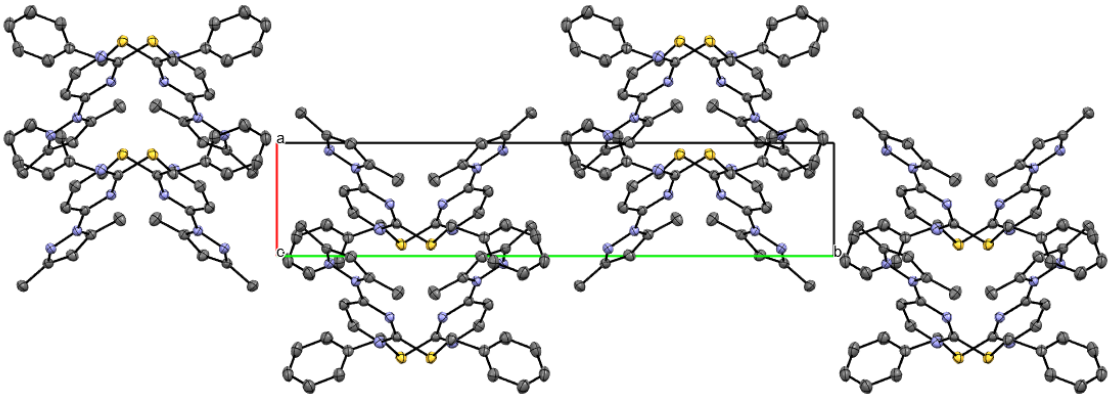


Figure S13. Packing of **L^{H}** (view along the *c* axis, hydrogen atoms are omitted for clarity).

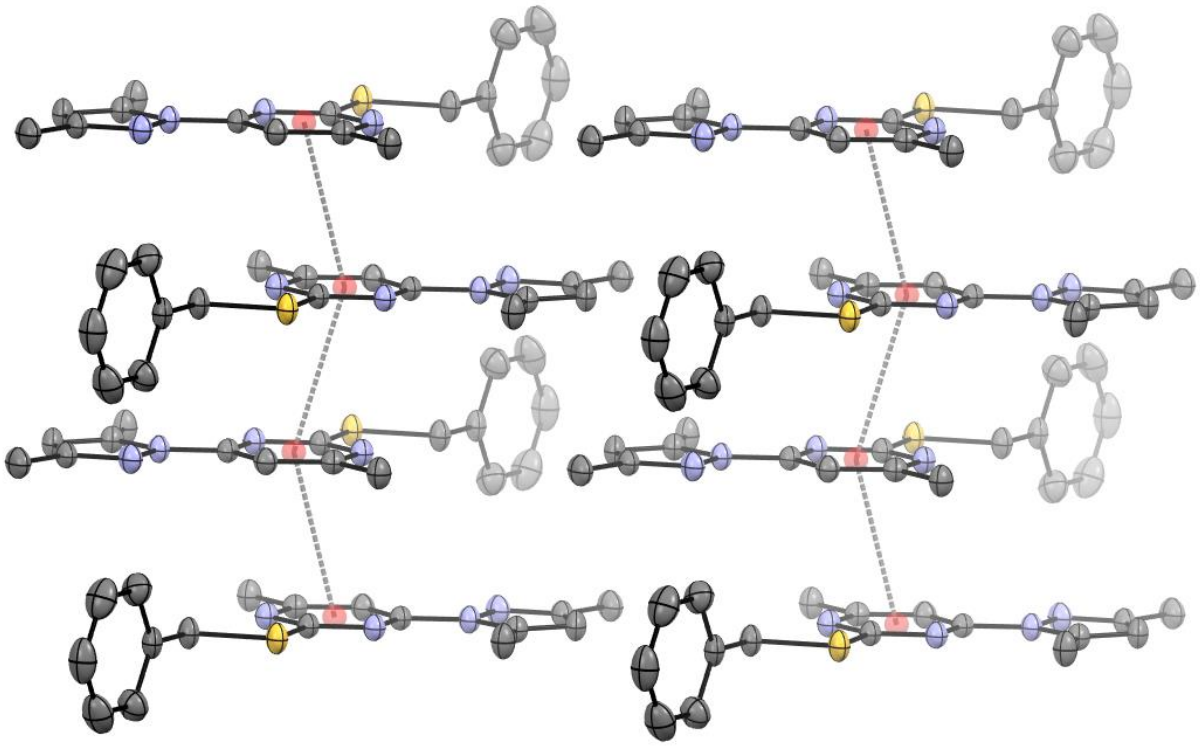


Figure S14. Supramolecular chains in the structure of **L^{Me}** (hydrogen atoms are omitted for clarity).

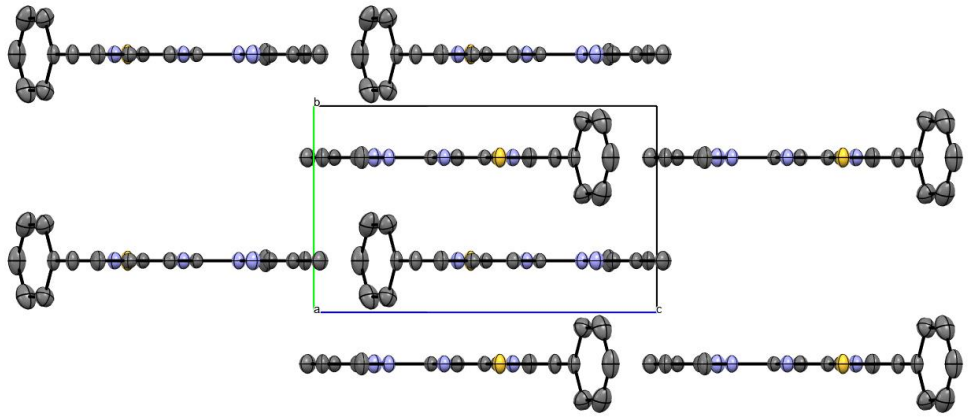


Figure S15. Packing of **L^{Me}** (view along the *a* axis, hydrogen atoms are omitted for clarity).

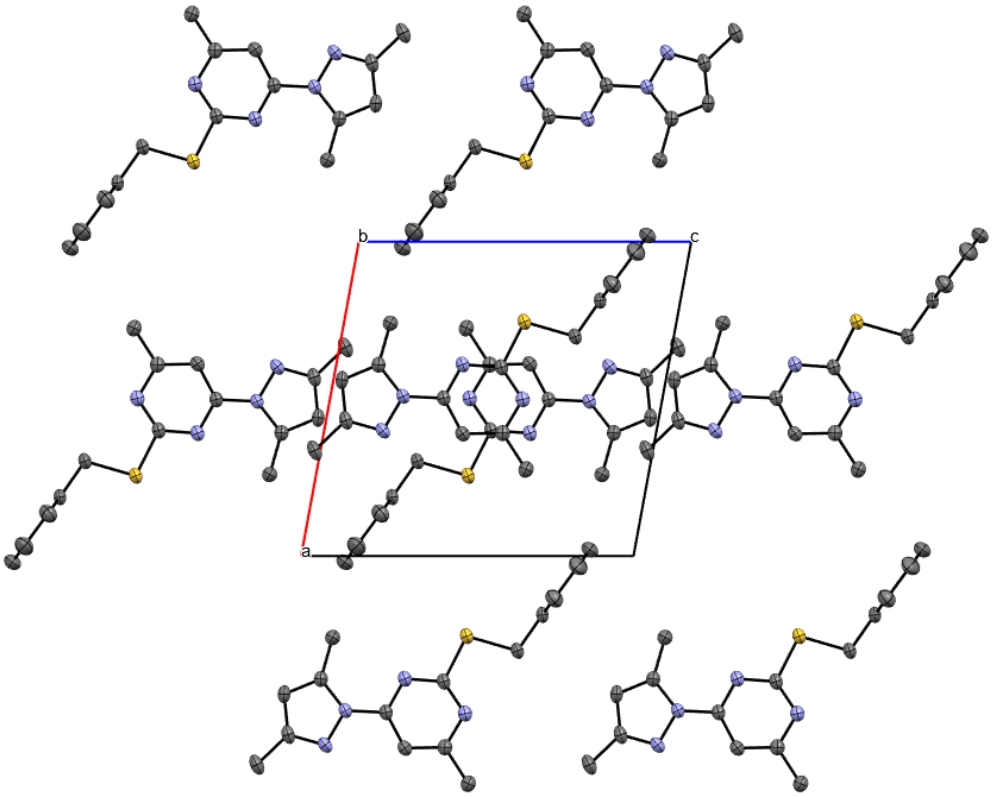


Figure S16. Packing of **L^{Me}** (view along the *b* axis, hydrogen atoms are omitted for clarity).

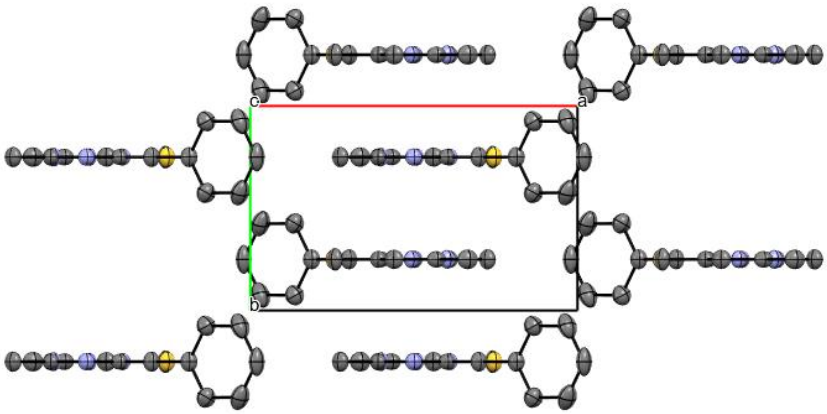


Figure S17. Packing of **L^{Me}** (view along the *c* axis, hydrogen atoms are omitted for clarity).

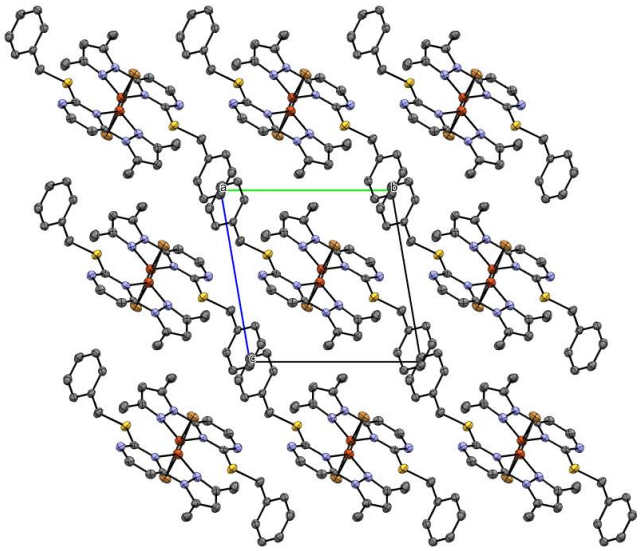


Figure S18. Packing of **$[Cu_2(L^H)_2Br_2]$** (view along the *a* axis, hydrogen atoms are omitted for clarity).

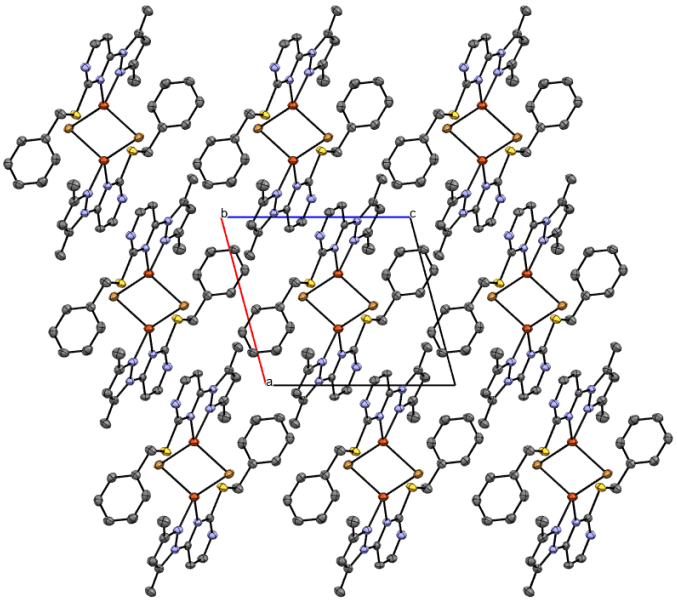


Figure S19. Packing of **$[Cu_2(L^H)_2Br_2]$** (view along the *b* axis, hydrogen atoms are omitted for clarity).

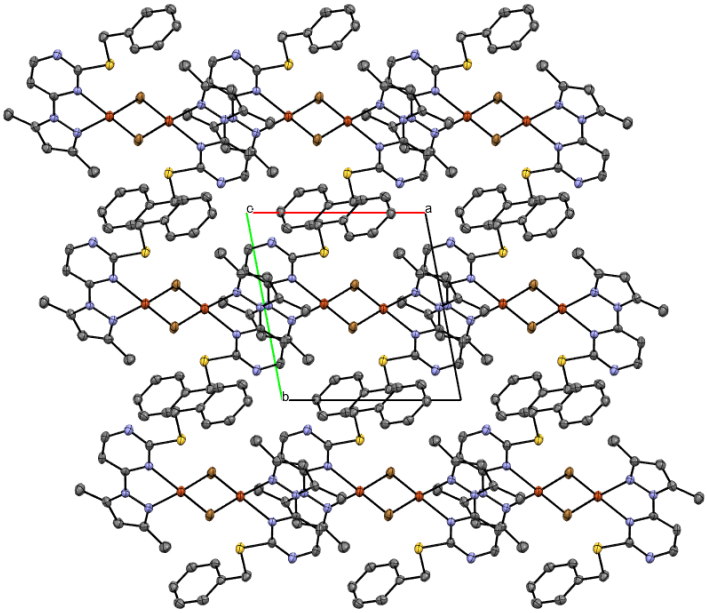


Figure S20. Packing of **$[Cu_2(L^H)_2Br_2]$** (view along the *c* axis, hydrogen atoms are omitted for clarity).

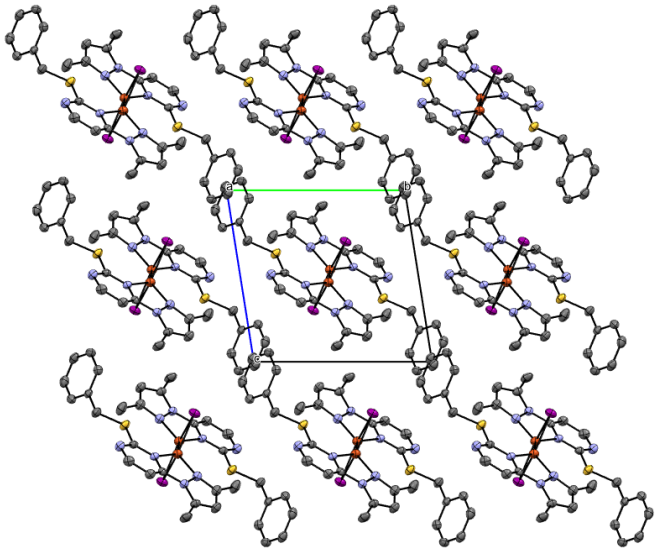


Figure S21. Packing of **$[Cu_2(L^H)_2I_2]$ (form I)** (view along the *a* axis, hydrogen atoms are omitted for clarity).

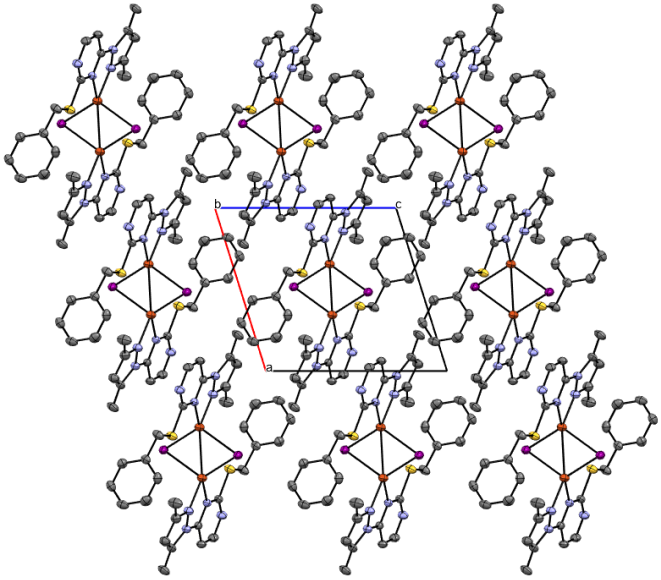


Figure S22. Packing of **$[Cu_2(L^H)_2I_2]$ (form I)** (view along the *b* axis, hydrogen atoms are omitted for clarity).

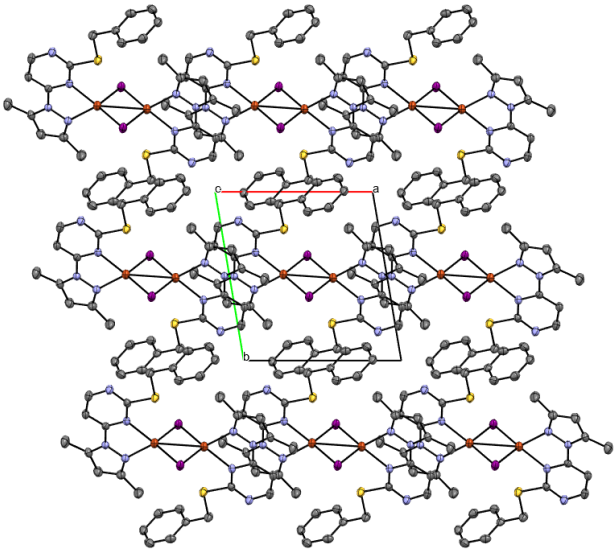


Figure S23. Packing of **$[Cu_2(L^H)_2I_2]$ (form I)** (view along the *c* axis, hydrogen atoms are omitted for clarity).

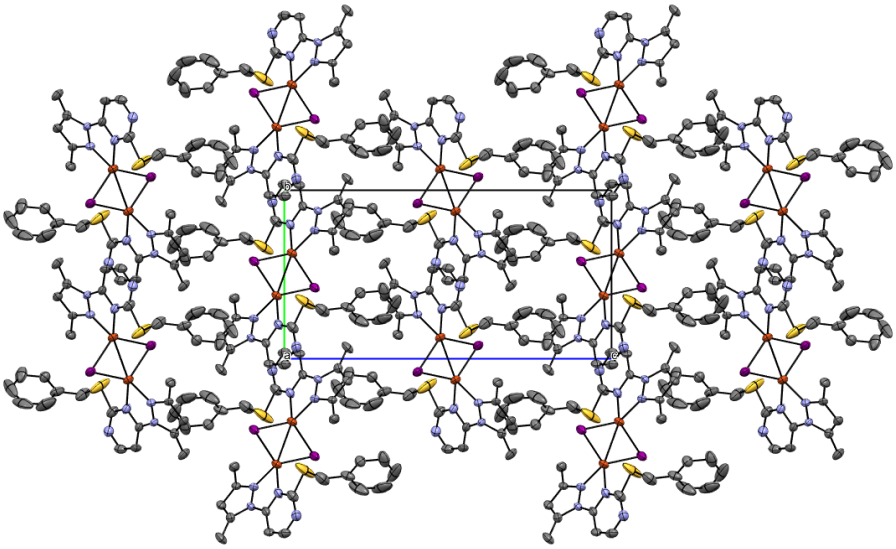


Figure S24. Packing of **$[Cu_2(L^H)_2I_2]$ (form II)** (view along the *a* axis, hydrogen atoms are omitted for clarity).

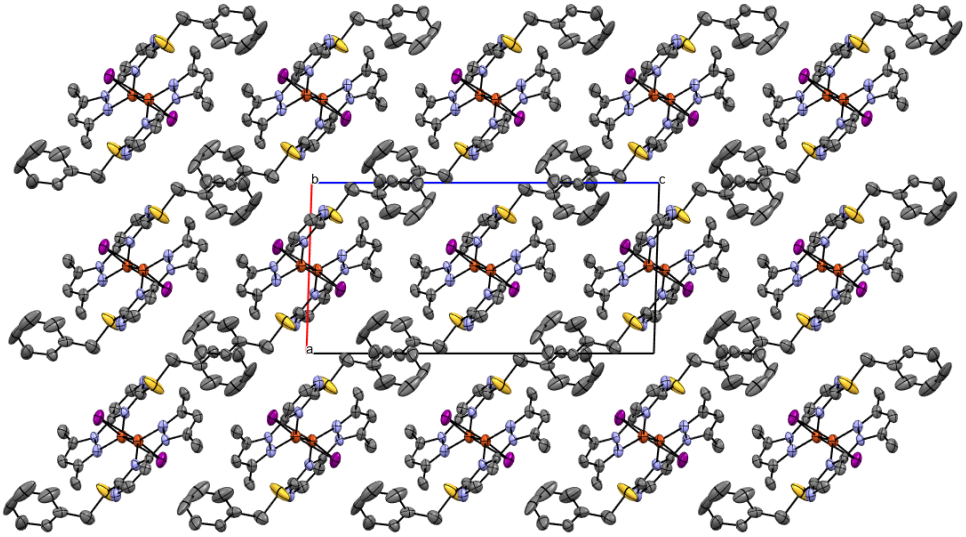


Figure S25. Packing of **$[Cu_2(L^H)_2I_2]$ (form II)** (view along the *b* axis, hydrogen atoms are omitted for clarity).

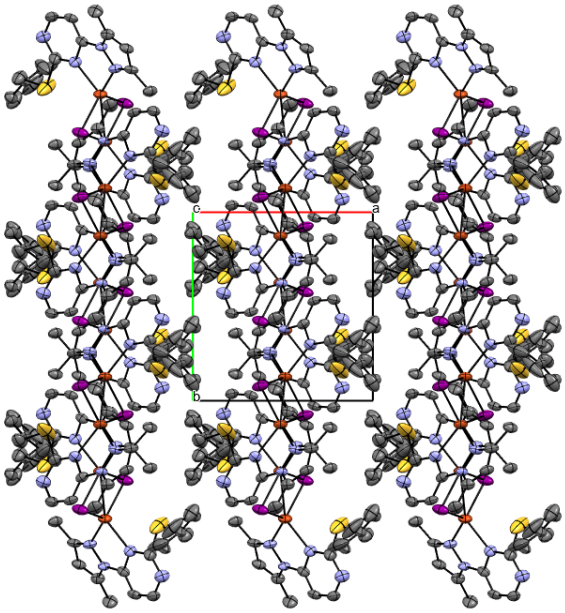


Figure S26. Packing of **$[Cu_2(L^H)_2I_2]$ (form II)** (view along the *c* axis, hydrogen atoms are omitted for clarity).

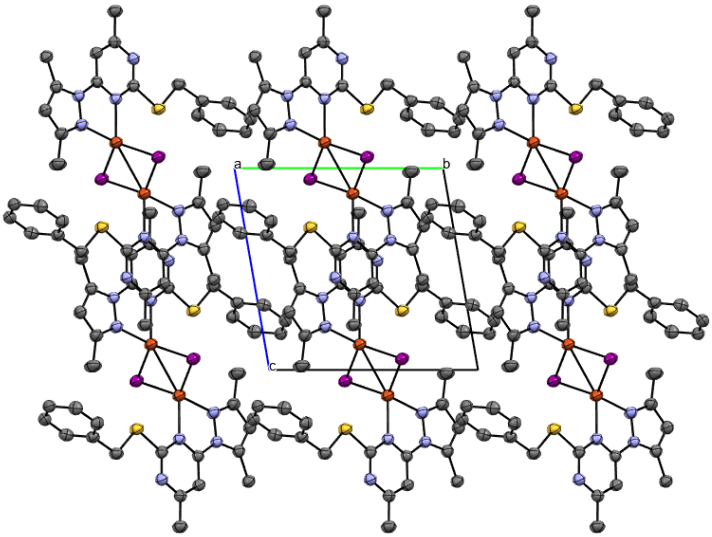


Figure S27. Packing of **[$Cu_2(L^{Me})_2I_2$]** (view along the *a* axis, hydrogen atoms are omitted for clarity).

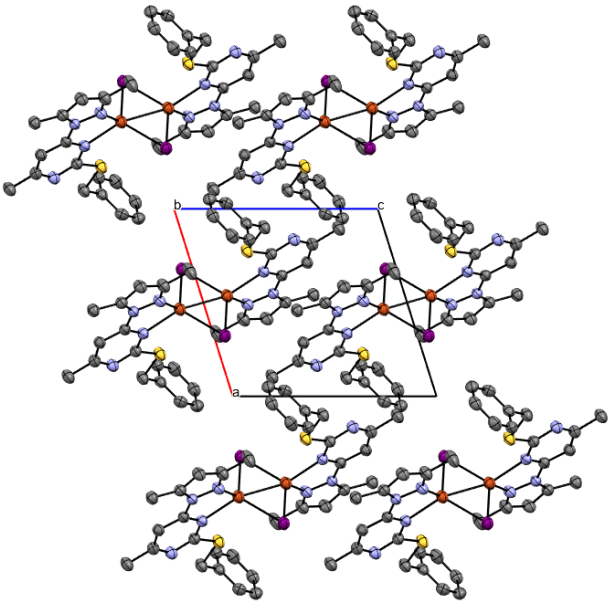


Figure S28. Packing of **[$Cu_2(L^{Me})_2I_2$]** (view along the *b* axis, hydrogen atoms are omitted for clarity).

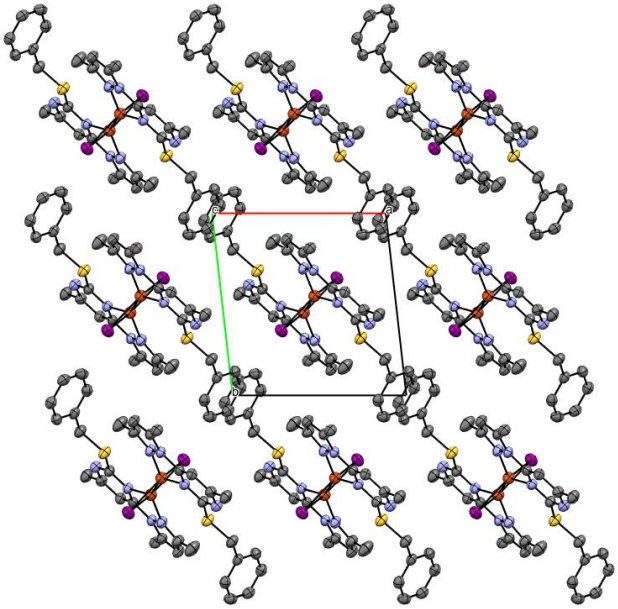


Figure S29. Packing of **[$Cu_2(L^{Me})_2I_2$]** (view along the *c* axis, hydrogen atoms are omitted for clarity).

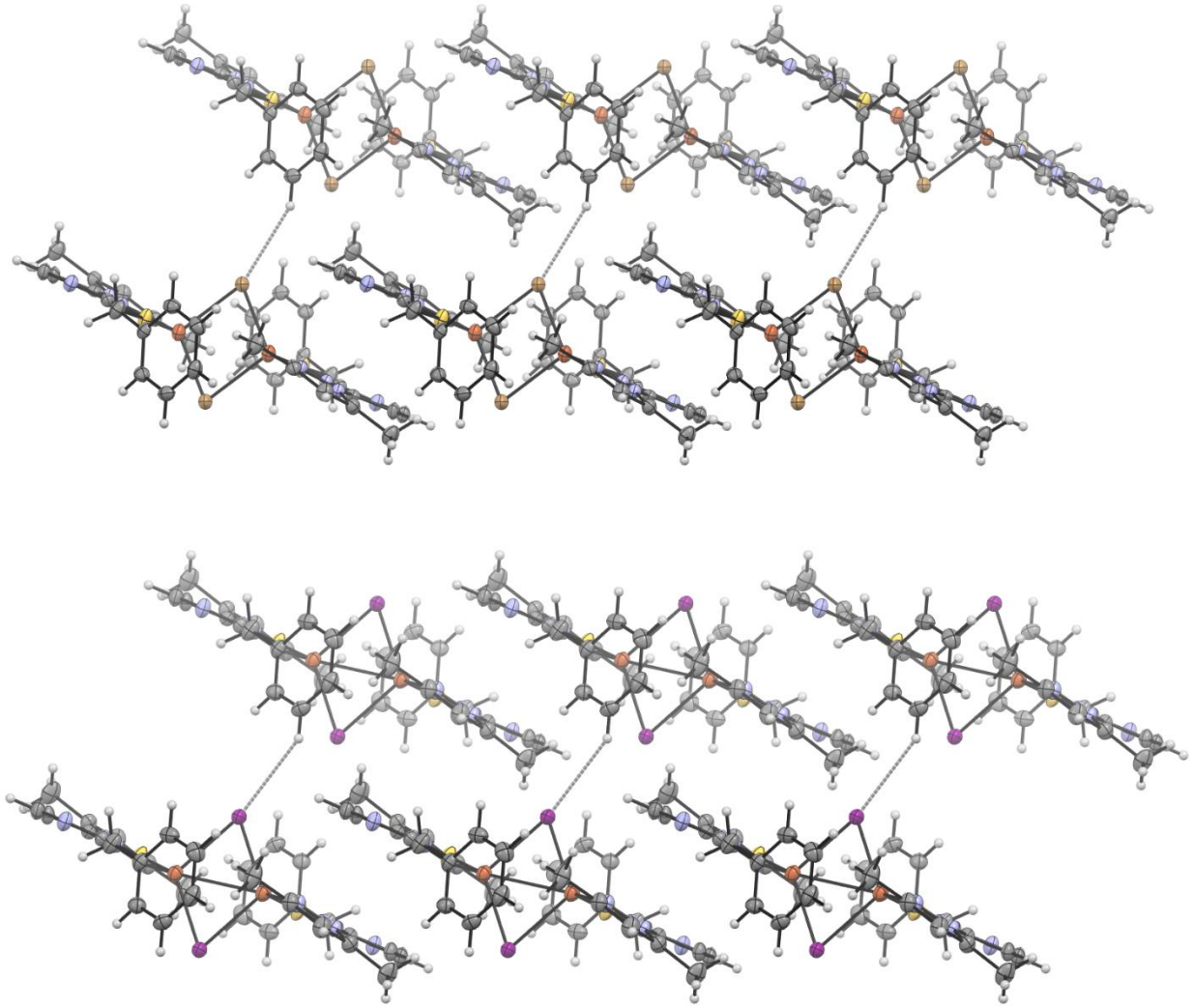


Figure S30. C–H···Hal interactions in the structures of **$[Cu_2(L^H)_2Br_2]$** and **$[Cu_2(L^H)_2I_2]$ (form I)**.

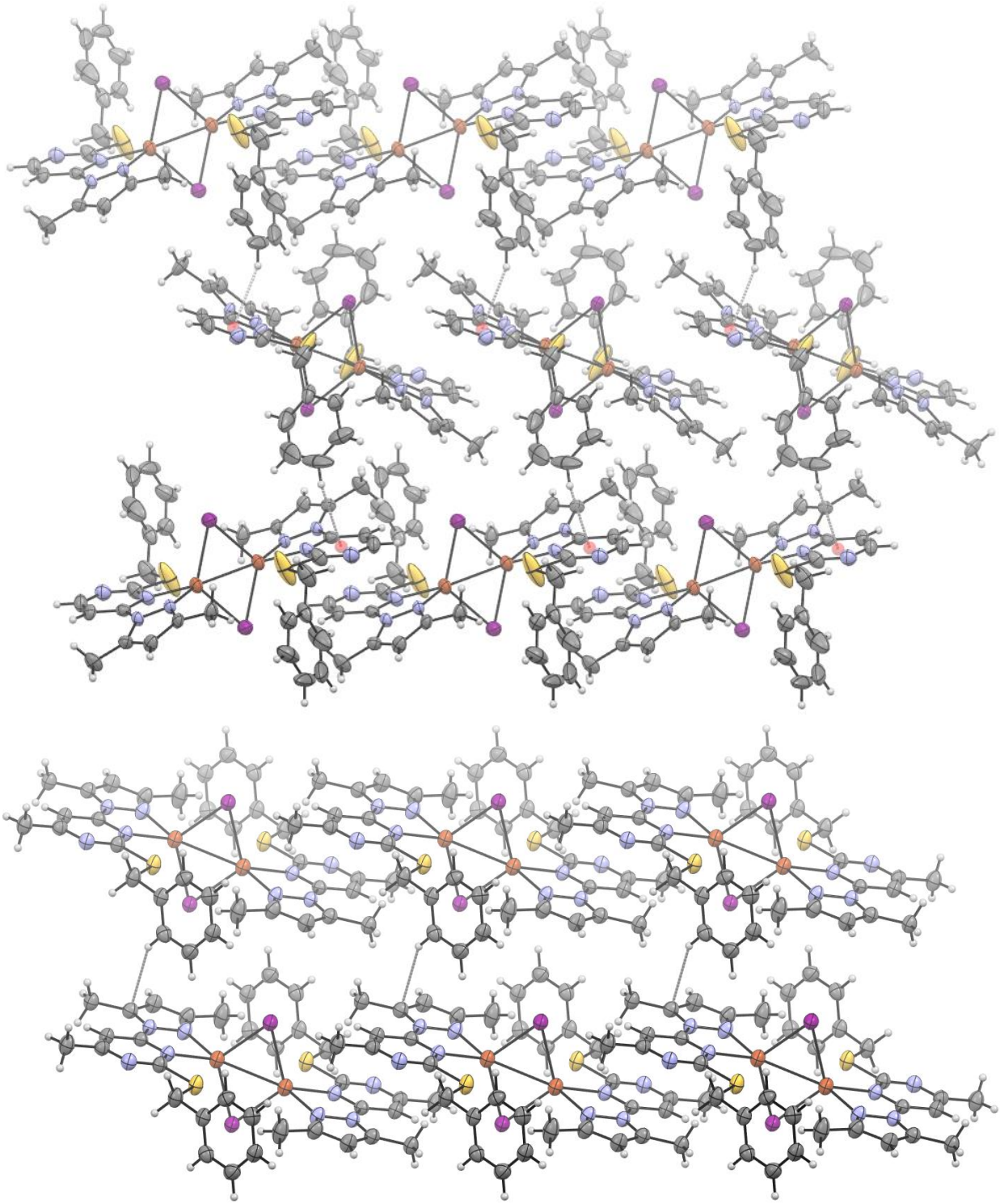


Figure S31. C–H···π interactions in the structure of **[$Cu_2(L^H)_2I_2$] (form II)** (top). C(Ph)–H···C(pz) interactions in the structure of **[$Cu_2(L^{Me})_2I_2$]** (bottom).

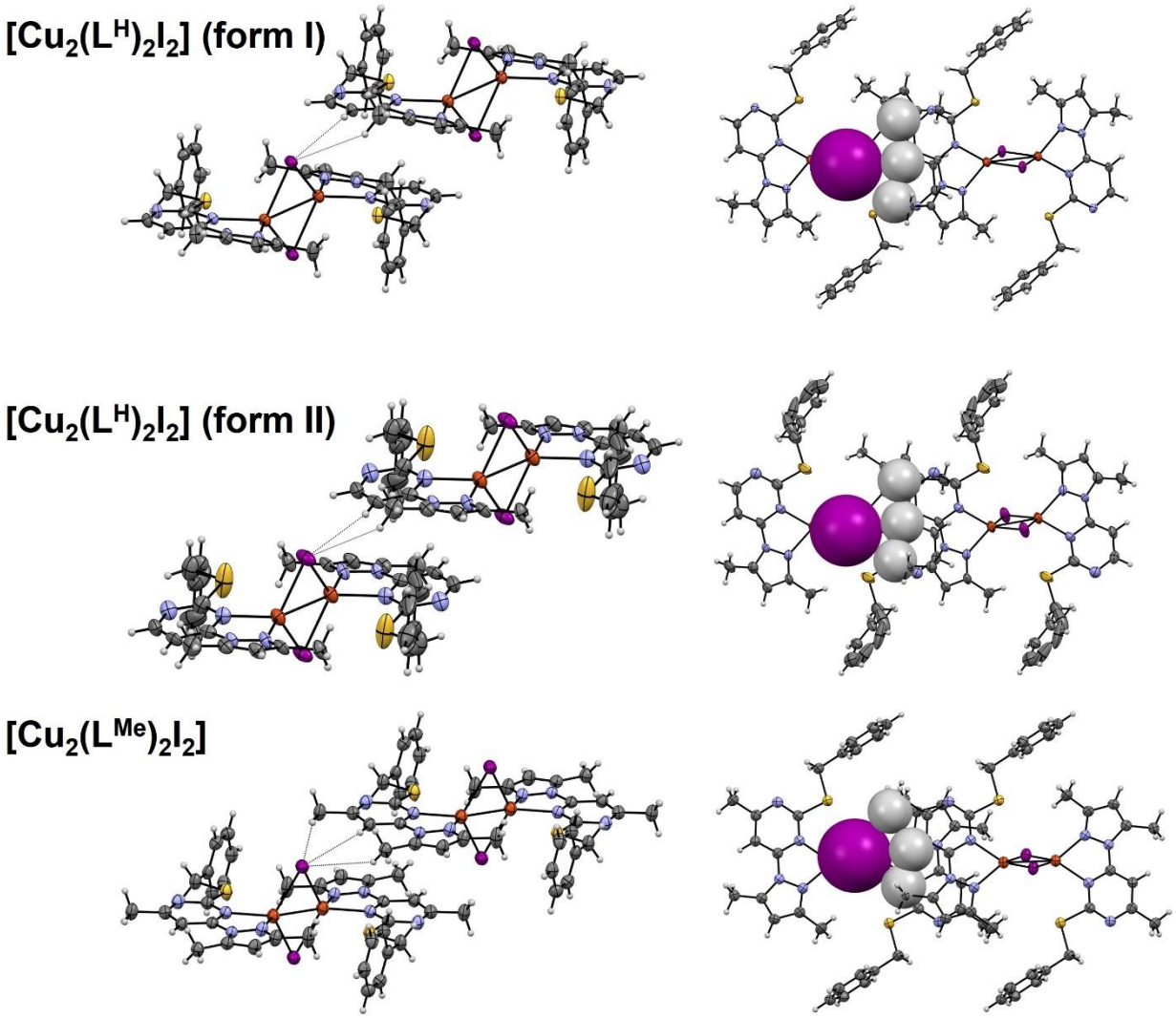
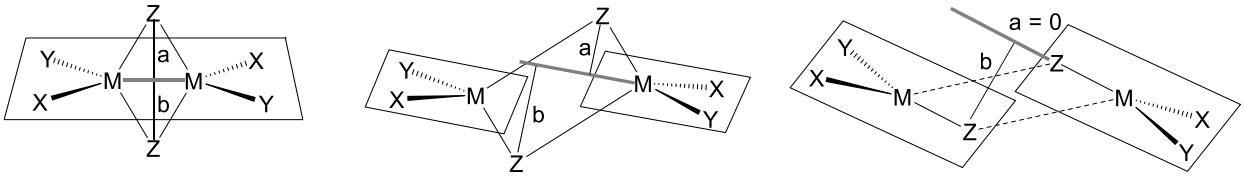


Figure S32. C–H···I contacts in the structures of **$[Cu_2(L^H)_2I_2]$ (form I)**, **$[Cu_2(L^H)_2I_2]$ (form II)** and **$[Cu_2(L^{Me})_2I_2]$**.



$\tau_{dim} = \frac{a}{b} = 1$ $0 < \tau_{dim} = \frac{a}{b} < 1$ $\tau_{dim} = \frac{a}{b} = 0$

Figure S33. **Different degrees of merging monomers into a centrosymmetric dimer evidenced by the parameter τ_{dim}.**

X-ray powder diffraction patterns

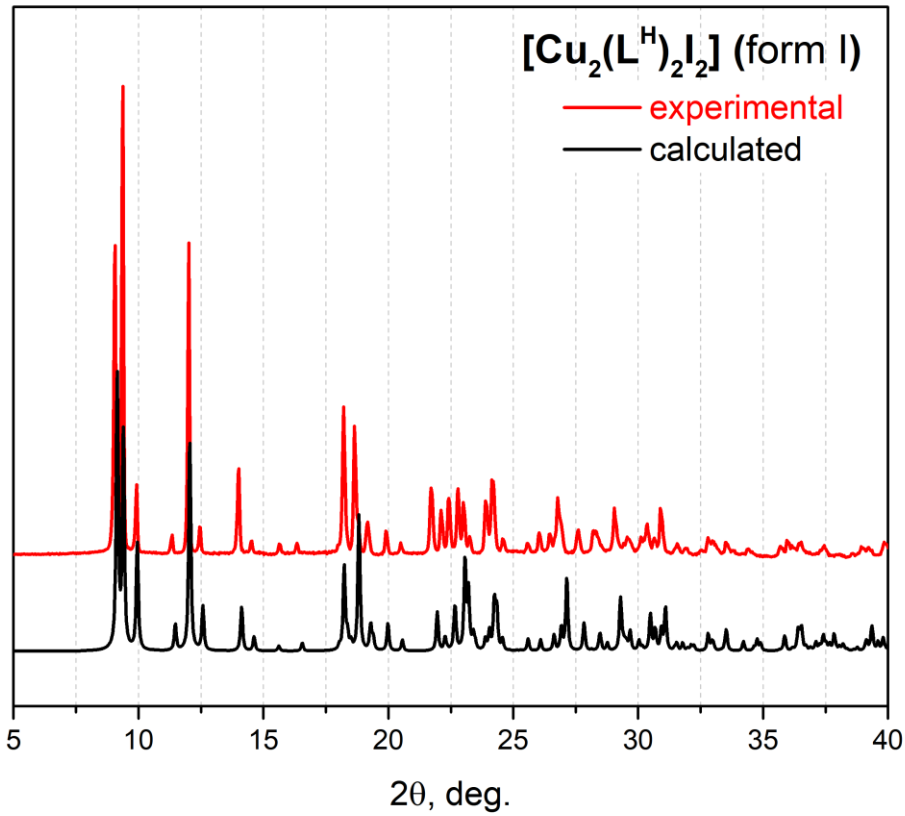


Figure S34. X-ray powder diffraction patterns of **$[Cu_2(L^H)_2I_2]$ (form I)**.

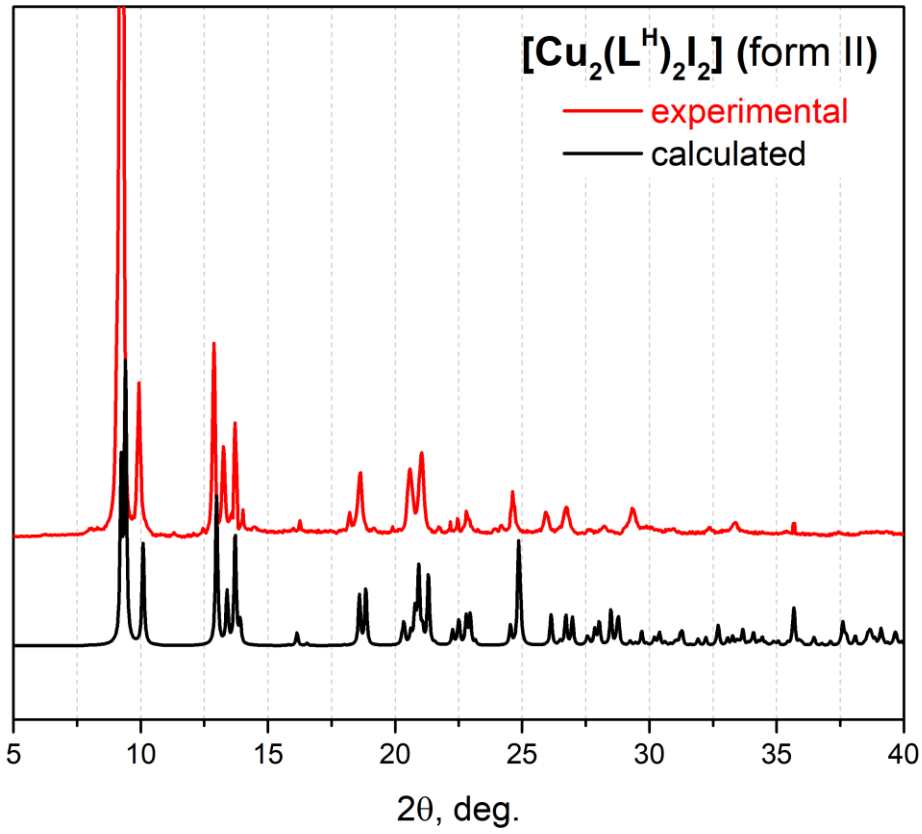


Figure S35. X-ray powder diffraction patterns of **$[Cu_2(L^H)_2I_2]$ (form II)**.

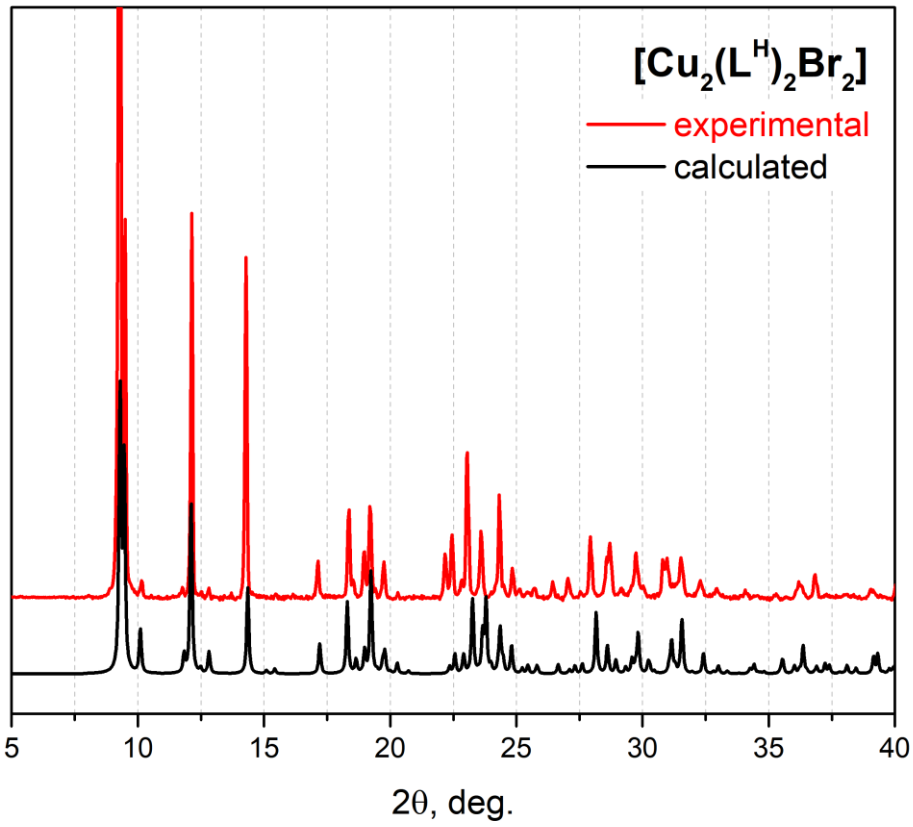


Figure S36. X-ray powder diffraction patterns of **$[Cu_2(L^H)_2Br_2]$**.

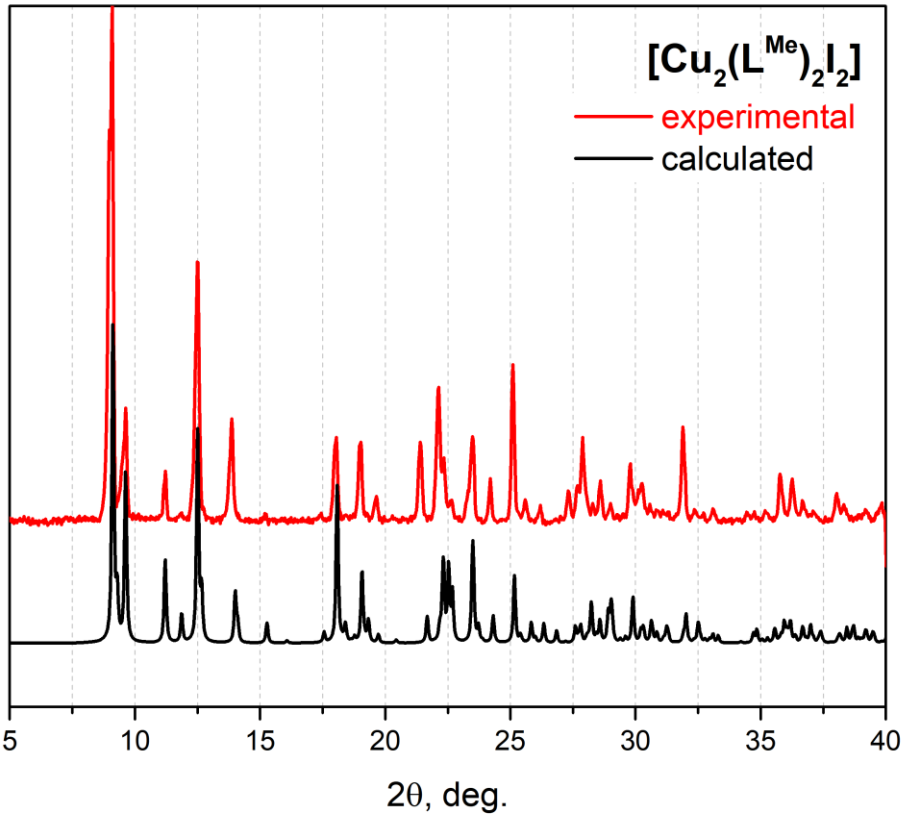


Figure S37. X-ray powder diffraction patterns of **$[Cu_2(L^{Me})_2I_2]$**.

IR spectra

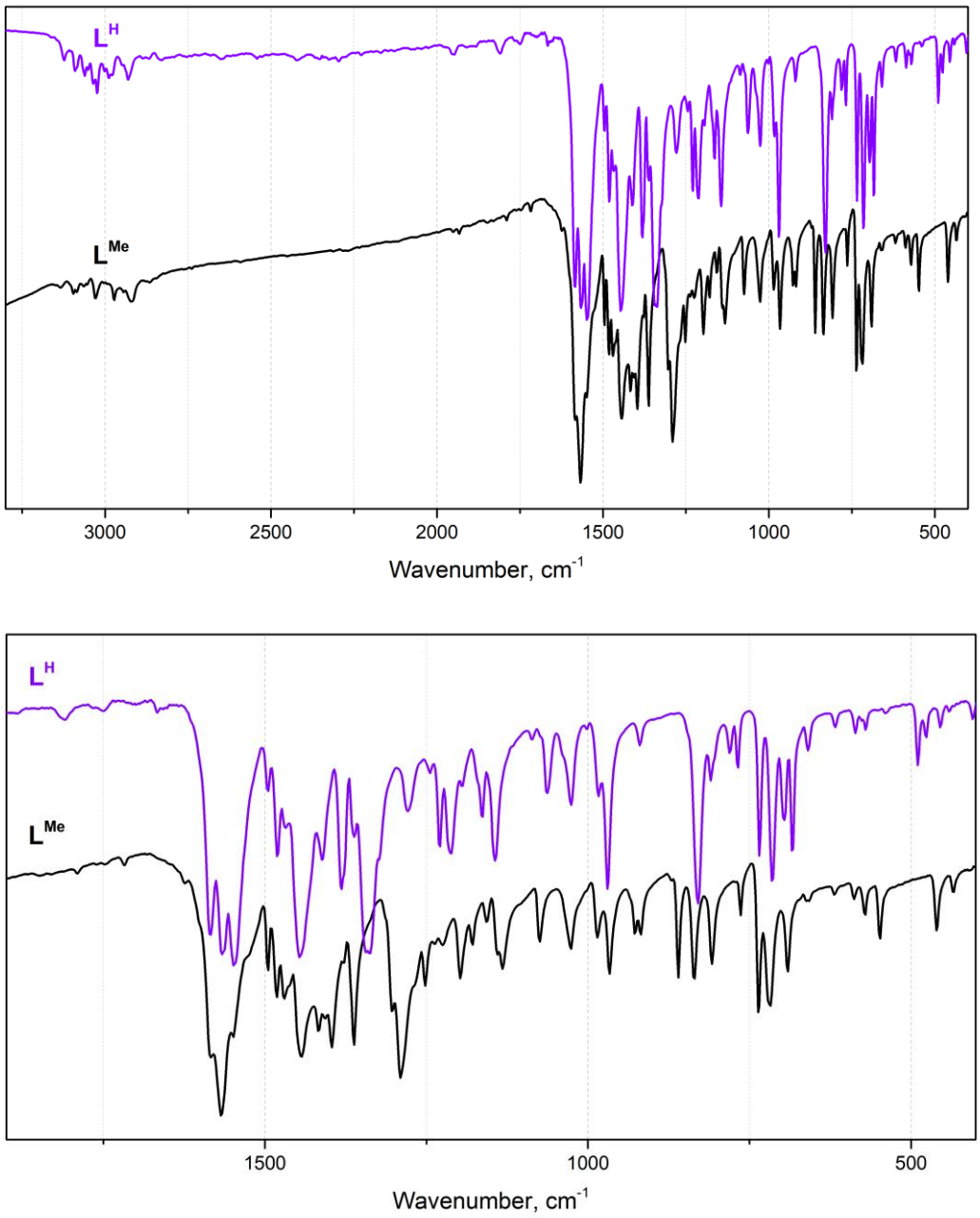


Figure S38. IR spectra of $\mathbf{L^H}$ and $\mathbf{L^{Me}}$.

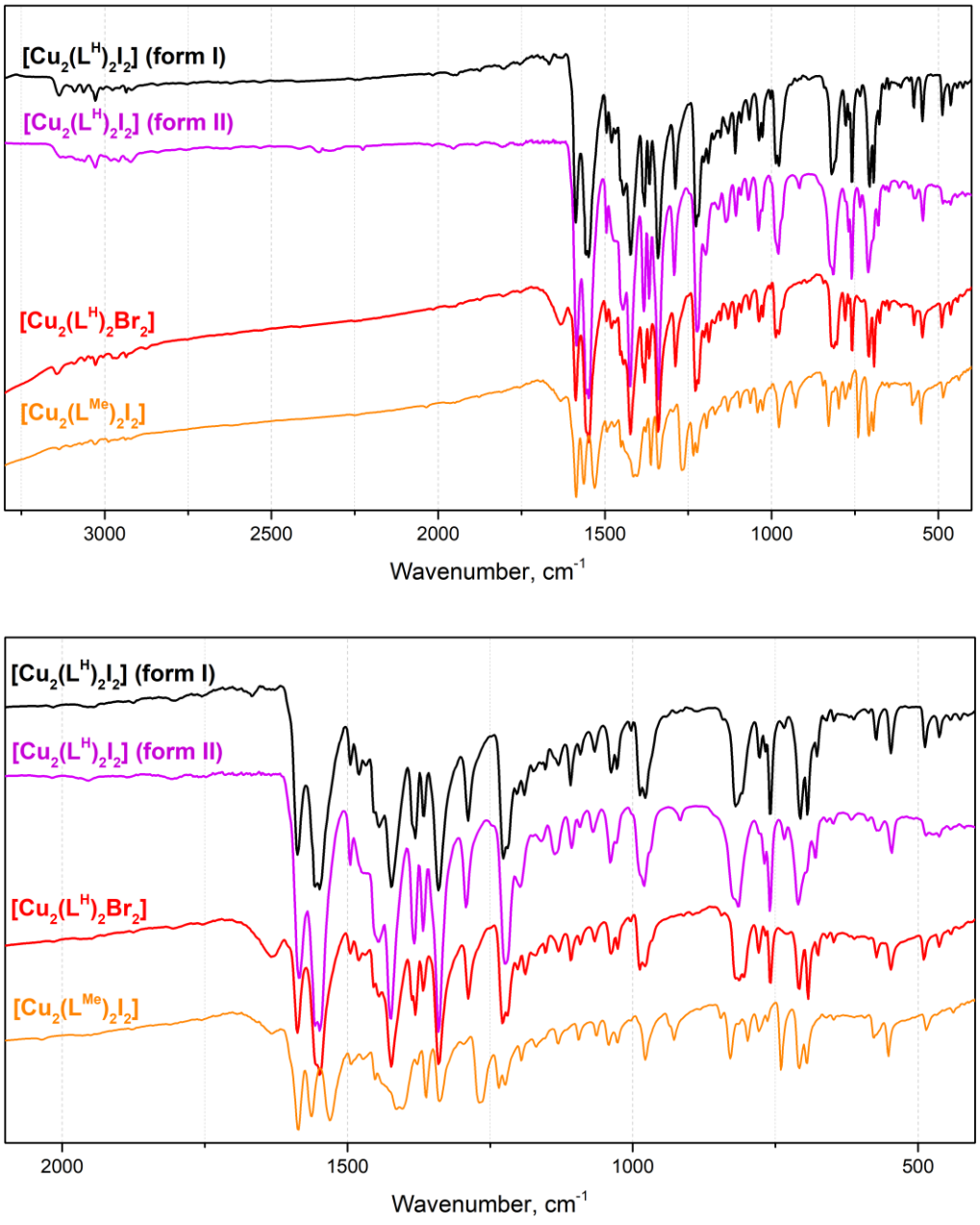


Figure S39. IR spectra of **$[Cu_2(L^H)_2I_2]$ (form I)**, **$[Cu_2(L^H)_2I_2]$ (form II)**, **$[Cu_2(L^H)_2Br_2]$** and **$[Cu_2(L^{Me})_2I_2]$**.

Diffuse reflectance spectra

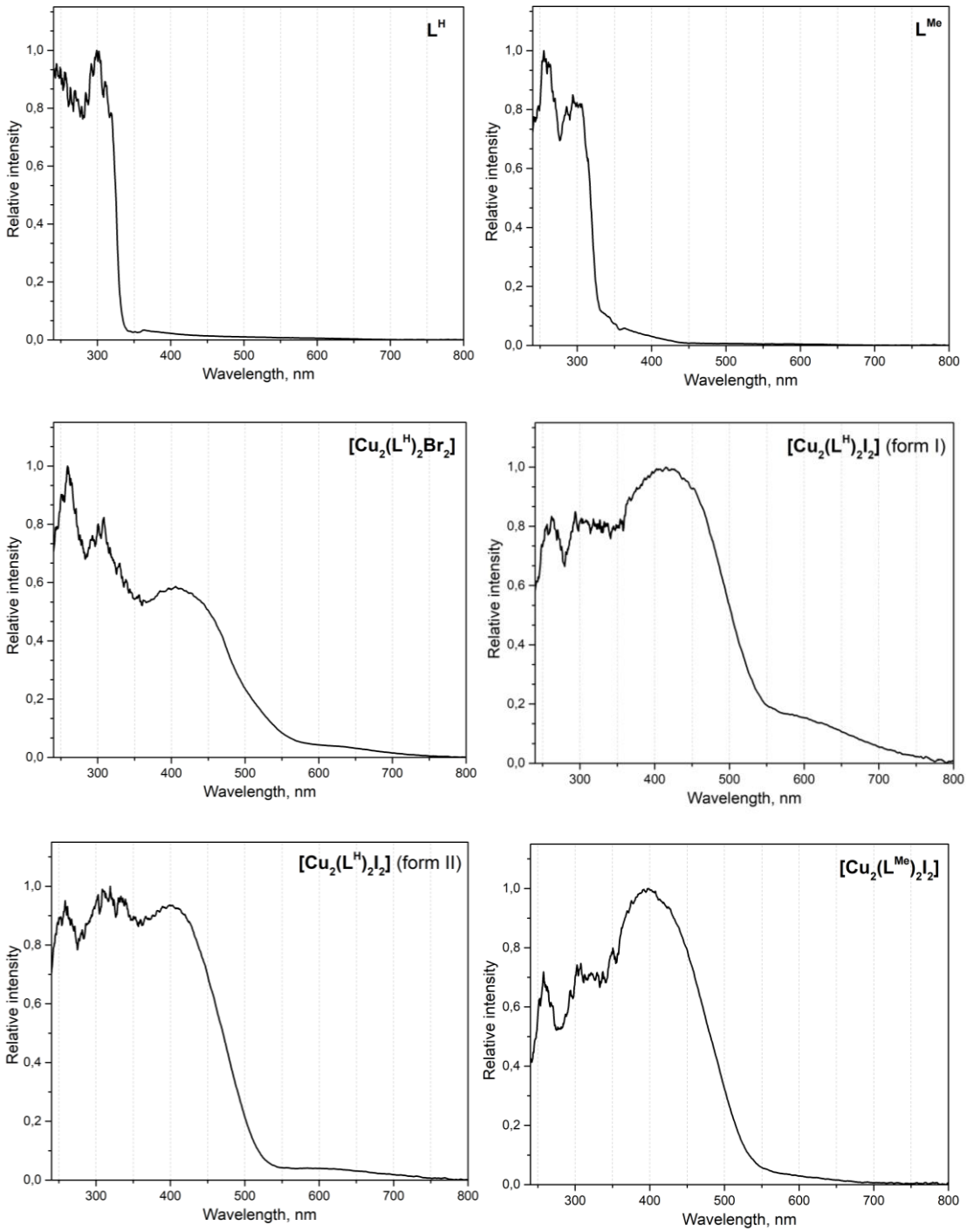


Figure S40. **Diffuse reflectance spectra.**

Computational data

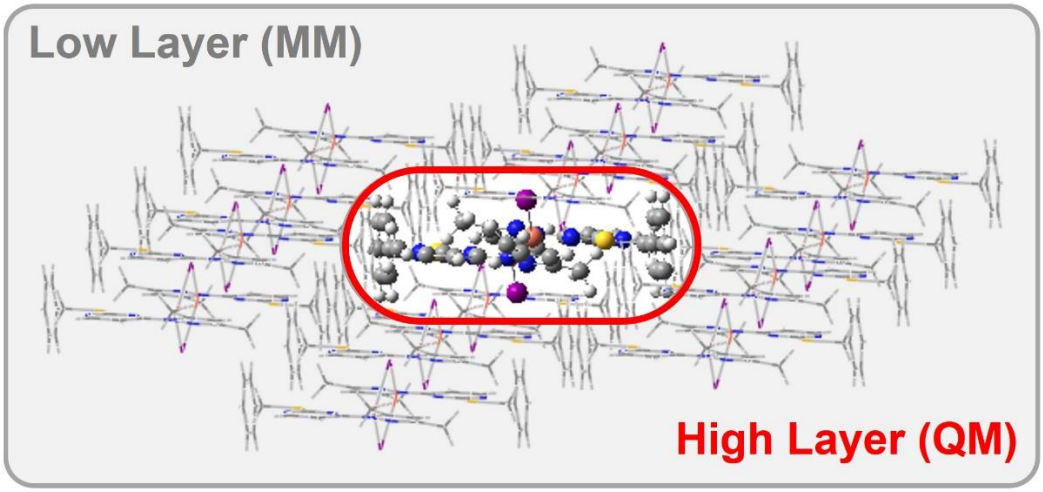


Figure S41. ONIOM model for the QM/MM calculation of the **$[Cu_2(L^H)_2I_2]$** complex (**form I**).

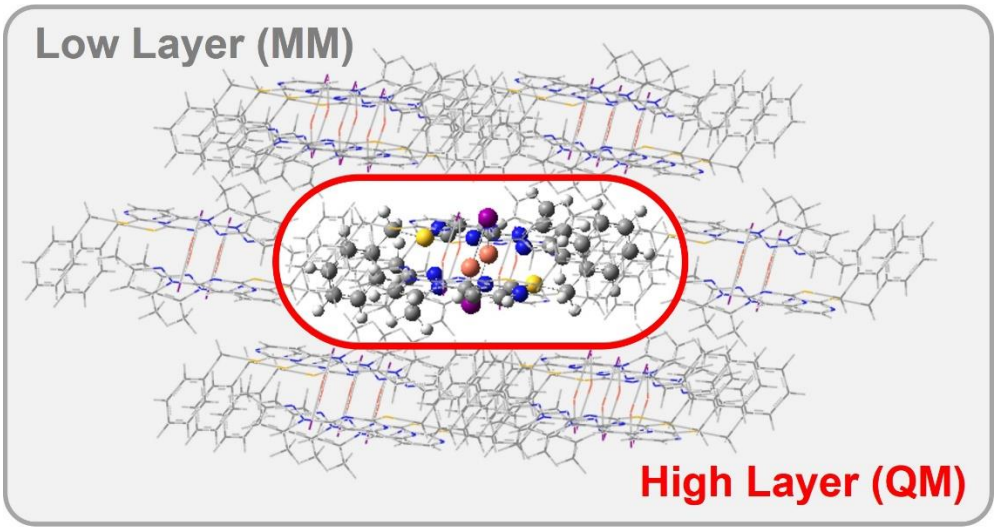


Figure S42. ONIOM model for the QM/MM calculation of the **$[Cu_2(L^H)_2I_2]$** complex (**form II**).

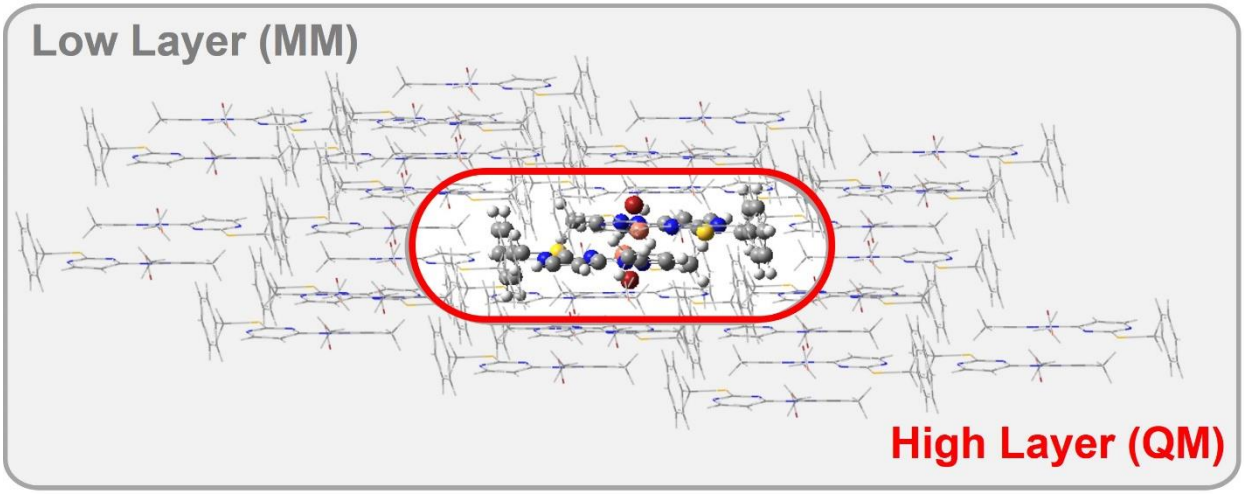


Figure S43. ONIOM model for the QM/MM calculation of the **$[Cu_2(L^H)_2Br_2]$** complex.

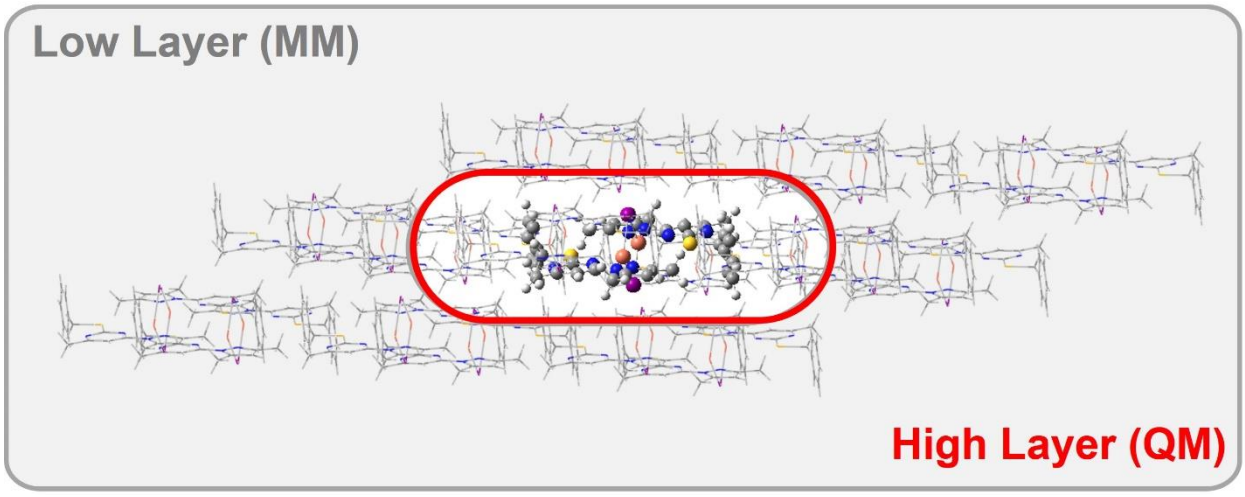


Figure S44. ONIOM model for the QM/MM calculation of the **$[Cu_2(L^{Me})_2I_2]$** complex.

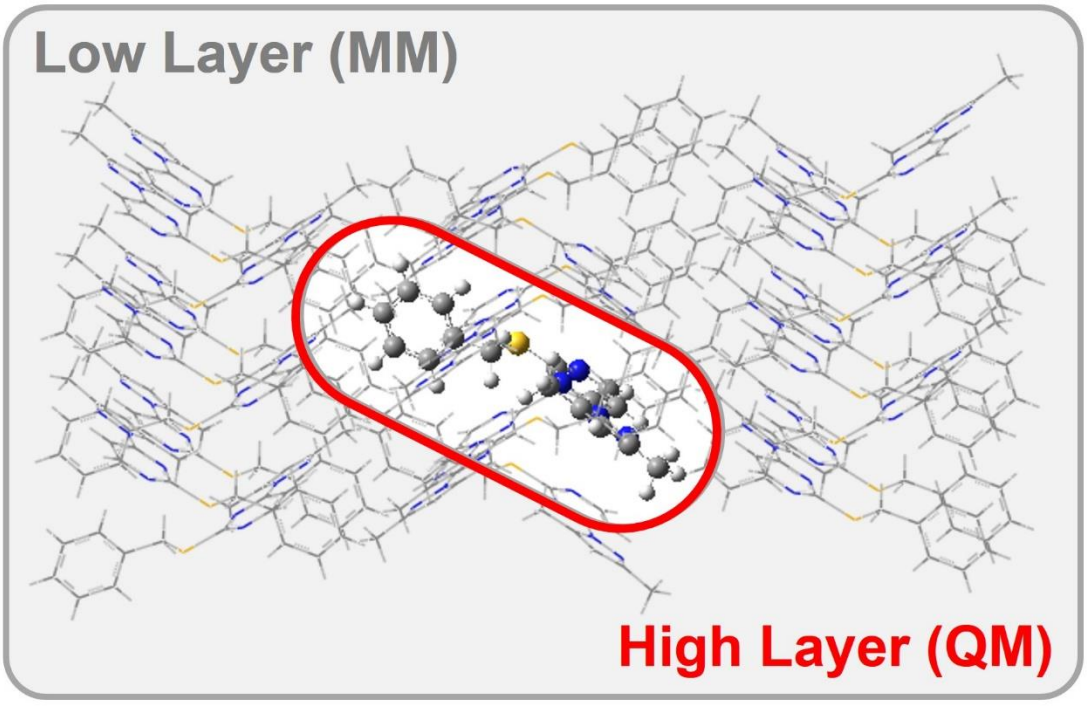


Figure S45. ONIOM model for the QM/MM calculation of **L^H**.

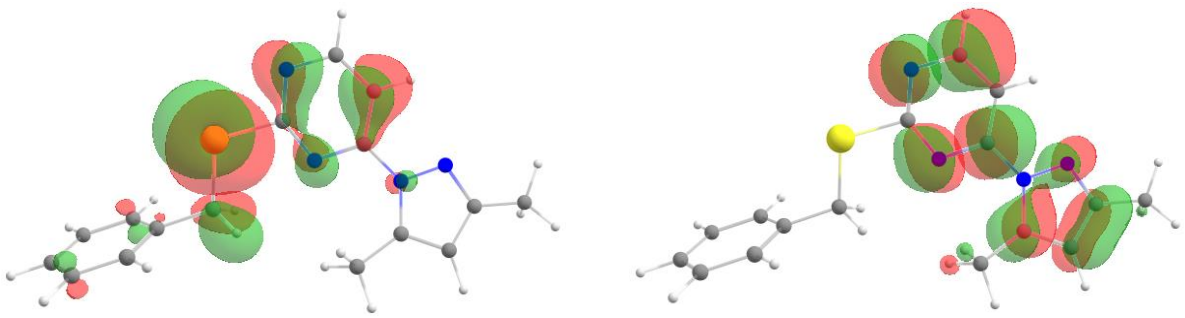
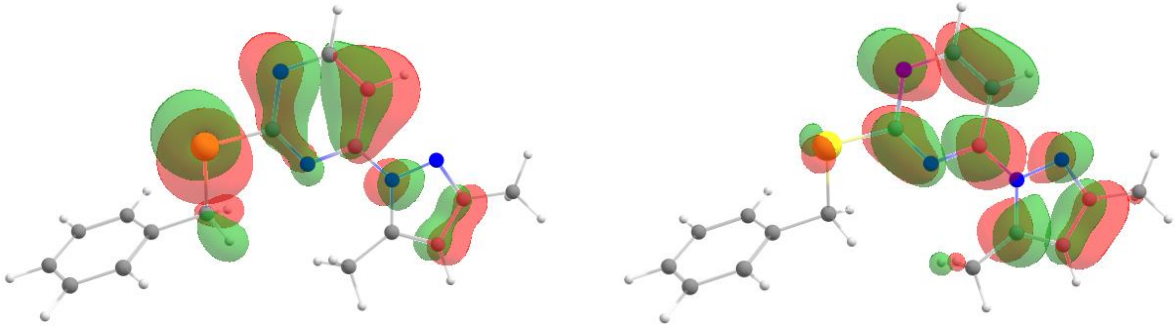
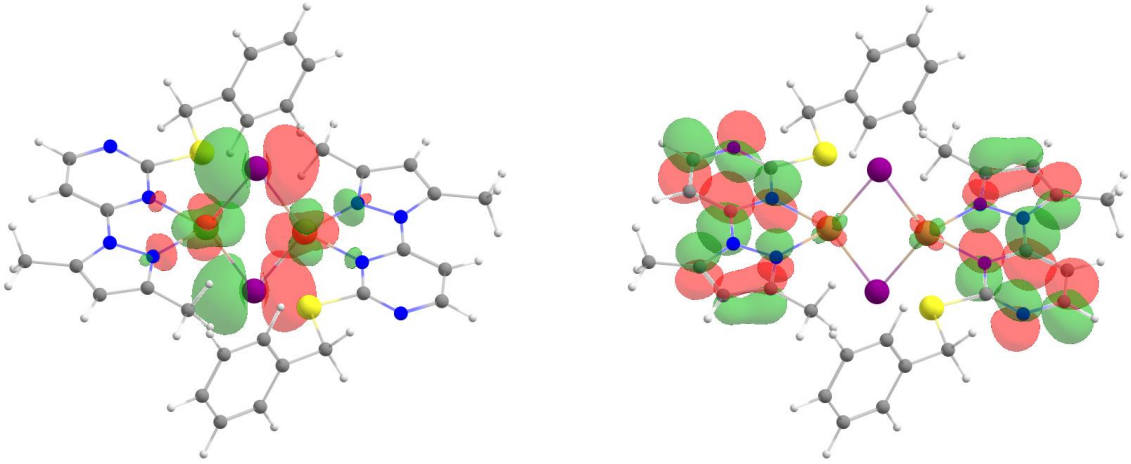


Figure S46. Frontier molecular orbitals of **L^H** at the S_1 optimized geometry.



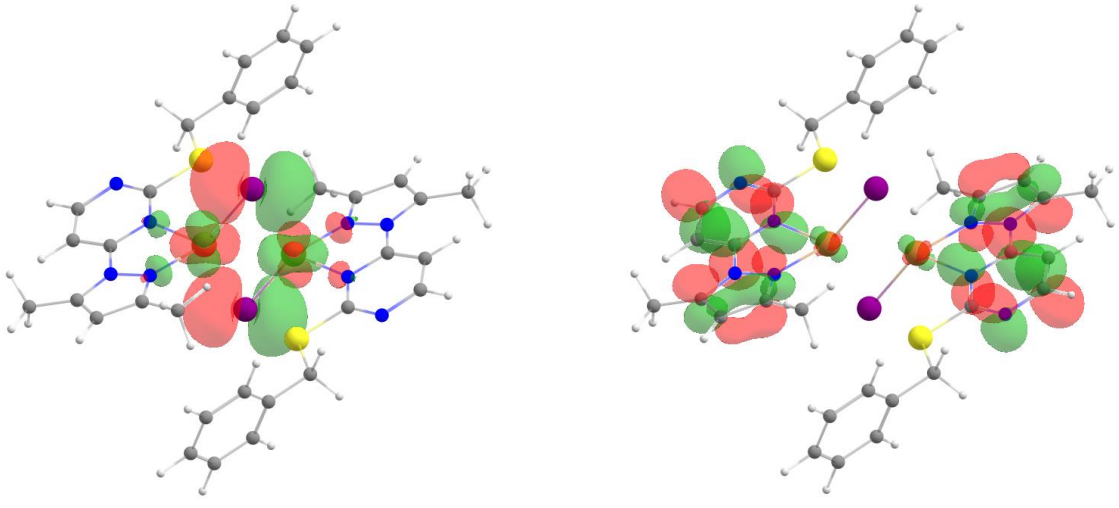
HOMO **LUMO**

Figure S47. Frontier molecular orbitals of $\mathbf{L^H}$ at the T_1 optimized geometry.



HOMO **LUMO**

Figure S48. Frontier molecular orbitals of the **$[Cu_2(L^H)_2I_2]$** complex (**phase I**, Cu…Cu 2.851 Å) at the T_1 optimized geometry.



HOMO **LUMO**

Figure S49. Frontier molecular orbitals of the **$[Cu_2(L^H)_2I_2]$** complex (**phase II**, Cu…Cu 2.619 Å) at the T_1 optimized geometry.

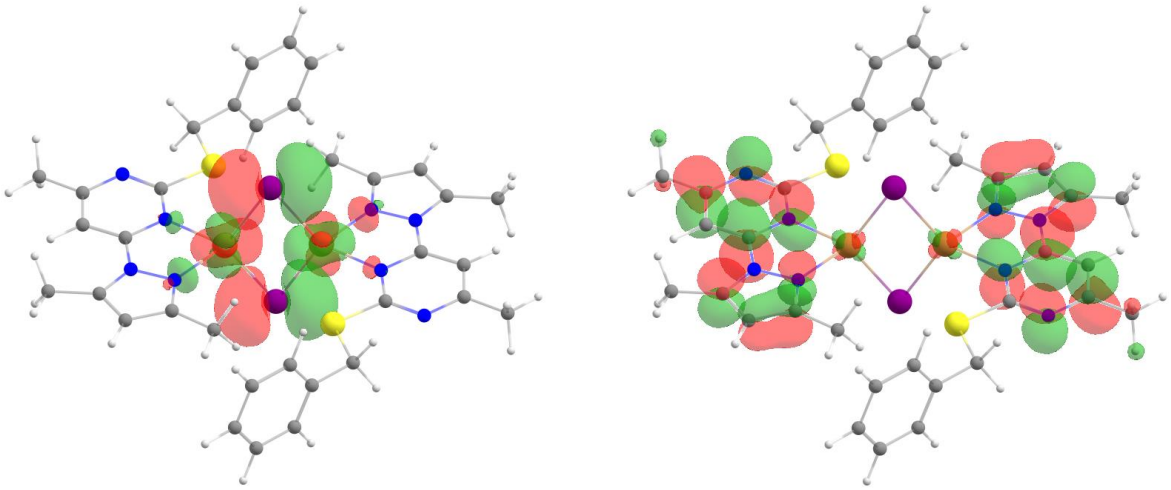


Figure S50. Frontier molecular orbitals of the **[$Cu_2(L^{Me})_2I_2$]** complex at the T_1 optimized geometry.

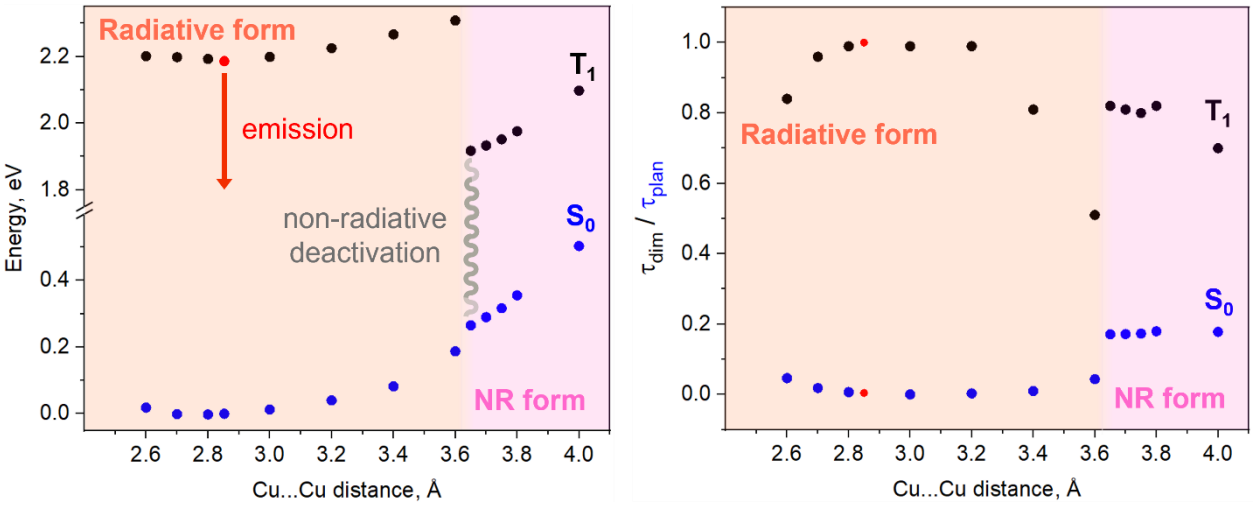


Figure S51. Energies of the T_1 and S_0 states (left) and the parameters τ_{dim} and τ_{plan} (right) of the **[$Cu_2(L^{Me})_2I_2$]** complex at the relaxed T_1 optimized geometries with fixed Cu…Cu distance. Areas corresponding to a particular phase (Radiative form, NR form) are marked with different colors.

Table S3. Optimized geometries of **L** in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory in QM/MM model.

Ground state (S_0)			
S	-0.566430000000	-0.200865000000	-0.060258000000
N	2.355150000000	-3.962142000000	-1.598232000000
N	1.030068000000	-2.164358000000	-0.928071000000
N	3.409109000000	-4.410219000000	-2.331880000000
N	1.645012000000	0.098104000000	-1.387118000000
C	2.114232000000	-2.585733000000	-1.574653000000
C	3.492633000000	-5.702190000000	-2.081415000000
C	0.850408000000	-0.843766000000	-0.876380000000
C	2.486436000000	-6.101886000000	-1.166731000000
H	2.319284000000	-7.092253000000	-0.771480000000
C	1.765327000000	-4.973196000000	-0.866825000000
C	-2.913907000000	-1.292025000000	0.708844000000

C	3.005264000000	-1.703927000000	-2.191047000000
H	3.872858000000	-2.059663000000	-2.724895000000
C	2.711138000000	-0.358507000000	-2.044494000000
H	3.369570000000	0.393363000000	-2.473728000000
C	4.534469000000	-6.549052000000	-2.726908000000
H	4.090332000000	-7.267289000000	-3.420133000000
H	5.078490000000	-7.140314000000	-1.985289000000
H	5.245543000000	-5.928963000000	-3.277739000000
C	-1.538646000000	-1.708389000000	0.270381000000
H	-1.573748000000	-2.297260000000	-0.650323000000
H	-1.038591000000	-2.304390000000	1.037742000000
C	-3.235918000000	-1.215805000000	2.065656000000
H	-2.480756000000	-1.475650000000	2.803791000000
C	-3.884474000000	-0.947523000000	-0.237046000000
H	-3.641134000000	-0.992247000000	-1.297130000000
C	-5.151745000000	-0.542536000000	0.168331000000
H	-5.893217000000	-0.278158000000	-0.578319000000
C	0.604151000000	-4.831040000000	0.051997000000
H	0.775236000000	-4.065245000000	0.811803000000
H	0.434748000000	-5.786992000000	0.551576000000
H	-0.307907000000	-4.548626000000	-0.481243000000
C	-5.466872000000	-0.474748000000	1.524938000000
H	-6.456368000000	-0.157389000000	1.842177000000
C	-4.506374000000	-0.814611000000	2.473970000000
H	-4.747711000000	-0.764103000000	3.532369000000
First singlet excited state (S_1)			
S	-0.517354000000	-0.220500000000	0.027057000000
N	2.394730000000	-3.974425000000	-1.595931000000
N	0.992752000000	-2.173899000000	-0.920436000000
N	3.447422000000	-4.414420000000	-2.336268000000
N	1.581086000000	0.115337000000	-1.412573000000
C	2.125921000000	-2.616617000000	-1.591407000000
C	3.549340000000	-5.715912000000	-2.082540000000
C	0.894562000000	-0.874347000000	-0.912424000000
C	2.555242000000	-6.126506000000	-1.177409000000
H	2.392676000000	-7.117923000000	-0.781935000000
C	1.818201000000	-4.994094000000	-0.872330000000
C	-2.941626000000	-1.249732000000	0.692815000000
C	2.953037000000	-1.687842000000	-2.253256000000
H	3.804843000000	-2.045947000000	-2.816259000000
C	2.664131000000	-0.346689000000	-2.171498000000
H	3.268568000000	0.405488000000	-2.662015000000
C	4.613367000000	-6.533083000000	-2.733881000000
H	4.223425000000	-7.131263000000	-3.561287000000
H	5.061361000000	-7.235886000000	-2.025345000000
H	5.400638000000	-5.886584000000	-3.130606000000
C	-1.572122000000	-1.663106000000	0.244656000000
H	-1.562776000000	-2.202829000000	-0.708756000000
H	-1.063468000000	-2.315059000000	0.964803000000
C	-3.260968000000	-1.204989000000	2.051465000000
H	-2.511016000000	-1.487597000000	2.786579000000
C	-3.907459000000	-0.890829000000	-0.251264000000
H	-3.670108000000	-0.928225000000	-1.313026000000
C	-5.175219000000	-0.493815000000	0.162178000000

H	-5.915888000000	-0.220026000000	-0.580583000000
C	0.664267000000	-4.874227000000	0.062822000000
H	0.808236000000	-4.081180000000	0.800432000000
H	0.555293000000	-5.819461000000	0.599768000000
H	-0.277879000000	-4.668146000000	-0.456962000000
C	-5.489089000000	-0.450738000000	1.518915000000
H	-6.478483000000	-0.140181000000	1.841426000000
C	-4.530842000000	-0.809975000000	2.464287000000
H	-4.774597000000	-0.782472000000	3.522575000000
First triplet excited state (T_1)			
S	-0.551675000000	-0.204151000000	-0.077519000000
N	2.376837000000	-3.999457000000	-1.579100000000
N	1.002121000000	-2.210553000000	-0.905653000000
N	3.432769000000	-4.412558000000	-2.333238000000
N	1.698876000000	0.117625000000	-1.327574000000
C	2.069845000000	-2.655273000000	-1.567110000000
C	3.554815000000	-5.712712000000	-2.091720000000
C	0.830915000000	-0.916431000000	-0.834759000000
C	2.568481000000	-6.146120000000	-1.177776000000
H	2.426173000000	-7.143354000000	-0.789974000000
C	1.820135000000	-5.034592000000	-0.854603000000
C	-2.936489000000	-1.257032000000	0.698524000000
C	2.959659000000	-1.698349000000	-2.270063000000
H	3.772439000000	-2.055934000000	-2.884380000000
C	2.701756000000	-0.349524000000	-2.073066000000
H	3.353271000000	0.396238000000	-2.524565000000
C	4.621760000000	-6.517008000000	-2.750430000000
H	4.225524000000	-7.127322000000	-3.565761000000
H	5.086376000000	-7.209779000000	-2.042828000000
H	5.394713000000	-5.864373000000	-3.163684000000
C	-1.568468000000	-1.678886000000	0.250286000000
H	-1.601551000000	-2.260809000000	-0.675726000000
H	-1.061461000000	-2.285941000000	1.005440000000
C	-3.250014000000	-1.185163000000	2.057648000000
H	-2.491314000000	-1.447139000000	2.791477000000
C	-3.913069000000	-0.916609000000	-0.241947000000
H	-3.678202000000	-0.964986000000	-1.303839000000
C	-5.178960000000	-0.516067000000	0.171497000000
H	-5.925207000000	-0.256293000000	-0.571440000000
C	0.675239000000	-4.909736000000	0.086184000000
H	0.822204000000	-4.098691000000	0.803264000000
H	0.572075000000	-5.844969000000	0.640010000000
H	-0.268552000000	-4.707460000000	-0.431522000000
C	-5.485783000000	-0.449863000000	1.529887000000
H	-6.474533000000	-0.136877000000	1.853138000000
C	-4.519063000000	-0.787848000000	2.473407000000
H	-4.754832000000	-0.740245000000	3.533133000000

Table S4. Optimized geometries of the **$[Cu_2(L^H)_2I_2]$** complex in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/Stuttgart RSC 1997/6-31+g(d) level of theory (ground state geometries - QM/MM model, triplet excited state geometries - gas phase).

Ground state (S_0), **phase I**			
C	-1.029897000000	5.241355000000	-0.391037000000
C	-2.268443000000	4.733307000000	-0.684657000000
H	-3.195395000000	5.286834000000	-0.659632000000
C	-2.084273000000	3.358814000000	-0.979817000000
C	1.227057000000	4.106494000000	-0.349206000000
C	2.044817000000	5.237767000000	-0.305724000000
H	1.657334000000	6.230108000000	-0.459274000000
C	3.392726000000	5.009467000000	-0.085146000000
H	4.091367000000	5.842445000000	-0.024504000000
C	3.057608000000	2.779487000000	-0.062444000000
C	5.413607000000	1.420487000000	0.355732000000
H	5.817087000000	2.031623000000	-0.456016000000
H	5.535048000000	1.973131000000	1.291436000000
C	6.057331000000	0.065826000000	0.414494000000
C	6.383152000000	-0.608200000000	-0.764754000000
H	6.199279000000	-0.126814000000	-1.722715000000
C	6.944186000000	-1.879597000000	-0.714587000000
H	7.228128000000	-2.377932000000	-1.632841000000
C	7.164918000000	-2.504728000000	0.509915000000
H	7.596279000000	-3.500850000000	0.538415000000
C	6.841421000000	-1.841514000000	1.691271000000
H	7.018710000000	-2.319434000000	2.650958000000
C	6.292297000000	-0.562896000000	1.638948000000
H	6.037395000000	-0.039669000000	2.555130000000
C	-0.690985000000	6.626350000000	0.039553000000
H	-0.040591000000	6.637345000000	0.919762000000
H	-1.619030000000	7.140111000000	0.302901000000
H	-0.210069000000	7.210852000000	-0.754071000000
C	-3.088104000000	2.343414000000	-1.389641000000
H	-3.538991000000	2.612792000000	-2.351971000000
H	-3.896603000000	2.268025000000	-0.654680000000
H	-2.611797000000	1.365060000000	-1.491921000000
Cu	0.268600000000	1.263284000000	-0.397202000000
I	0.548116000000	-0.699036000000	-2.068029000000
N	-0.154662000000	4.181790000000	-0.519734000000
N	-0.808864000000	3.040491000000	-0.862225000000
N	1.731191000000	2.878966000000	-0.246985000000
N	3.918457000000	3.792453000000	0.049462000000
S	3.636518000000	1.140199000000	0.046533000000
C	1.030250000000	-5.241376000000	0.390968000000
C	2.268808000000	-4.733367000000	0.684586000000
H	3.195736000000	-5.286916000000	0.659471000000
C	2.084682000000	-3.358889000000	0.979835000000
C	-1.226669000000	-4.106417000000	0.349188000000
C	-2.044496000000	-5.237644000000	0.305615000000
H	-1.657099000000	-6.230052000000	0.458978000000
C	-3.392409000000	-5.009223000000	0.085194000000
H	-4.091116000000	-5.842146000000	0.024586000000

C	-3.057147000000	-2.779263000000	0.062599000000
C	-5.413120000000	-1.420281000000	-0.355328000000
H	-5.816489000000	-2.031261000000	0.456590000000
H	-5.534659000000	-1.973122000000	-1.290904000000
C	-6.056957000000	-0.065676000000	-0.414290000000
C	-6.383017000000	0.608415000000	0.764858000000
H	-6.199116000000	0.127177000000	1.722888000000
C	-6.944340000000	1.879682000000	0.714508000000
H	-7.228478000000	2.378045000000	1.632688000000
C	-7.165153000000	2.504612000000	-0.510083000000
H	-7.596759000000	3.500625000000	-0.538744000000
C	-6.841398000000	1.841340000000	-1.691335000000
H	-7.018758000000	2.319097000000	-2.651091000000
C	-6.291971000000	0.562858000000	-1.638829000000
H	-6.036920000000	0.039572000000	-2.554935000000
C	0.691287000000	-6.626348000000	-0.039655000000
H	0.040857000000	-6.637316000000	-0.919838000000
H	1.619310000000	-7.140120000000	-0.303060000000
H	0.210394000000	-7.210855000000	0.753985000000
C	3.088575000000	-2.343565000000	1.389694000000
H	3.539380000000	-2.612958000000	2.352061000000
H	3.897133000000	-2.268285000000	0.654789000000
H	2.612362000000	-1.365161000000	1.491920000000
Cu	-0.268138000000	-1.263362000000	0.397311000000
I	-0.547867000000	0.698939000000	2.068081000000
N	0.155052000000	-4.181792000000	0.519712000000
N	0.809271000000	-3.040536000000	0.862286000000
N	-1.730734000000	-2.878849000000	0.247110000000
N	-3.918073000000	-3.792167000000	-0.049275000000
S	-3.635988000000	-1.139947000000	-0.046398000000
Ground state (S_0), **phase II**			
I	1.096946000000	-0.723552000000	1.861605000000
Cu	0.477340000000	-1.032120000000	-0.662039000000
N	0.921188000000	-3.462416000000	-2.299177000000
N	0.010402000000	-2.947664000000	-1.430436000000
N	2.198559000000	-1.593304000000	-1.875547000000
N	4.450034000000	-1.339002000000	-2.611430000000
C	-1.084735000000	-3.674203000000	-1.562500000000
C	2.153461000000	-2.813673000000	-2.403086000000
C	3.268417000000	-3.380470000000	-3.026330000000
H	3.266899000000	-4.382728000000	-3.418957000000
C	0.391682000000	-4.516094000000	-3.014014000000
C	-0.890704000000	-4.666099000000	-2.552163000000
H	-1.609240000000	-5.391090000000	-2.905034000000
C	-2.296737000000	-3.393630000000	-0.748862000000
H	-2.084692000000	-3.533610000000	0.317123000000
H	-3.120115000000	-4.053979000000	-1.033247000000
H	-2.615423000000	-2.355768000000	-0.892450000000
C	4.400629000000	-2.582572000000	-3.085873000000
H	5.316447000000	-2.959247000000	-3.538274000000
C	5.886445000000	3.301173000000	-0.549350000000
H	5.524679000000	4.006727000000	-1.293341000000
C	5.588704000000	1.945434000000	-0.690668000000
C	1.062651000000	-5.290826000000	-4.092631000000

H	1.530531000000	-4.648290000000	-4.846336000000
H	0.304972000000	-5.899514000000	-4.592565000000
H	1.820131000000	-5.978810000000	-3.700840000000
C	6.653374000000	3.752489000000	0.523433000000
H	6.903885000000	4.804734000000	0.613327000000
C	3.335053000000	-0.895849000000	-2.032496000000
C	6.798804000000	1.498766000000	1.359649000000
H	7.138159000000	0.792852000000	2.111197000000
C	6.031715000000	1.051698000000	0.290460000000
H	5.771596000000	-0.000378000000	0.209015000000
C	7.127917000000	2.849906000000	1.466996000000
H	7.760216000000	3.203517000000	2.273068000000
S	3.202233000000	0.739984000000	-1.438272000000
C	4.815580000000	1.462925000000	-1.885067000000
H	5.355399000000	0.687190000000	-2.436661000000
H	4.611920000000	2.288316000000	-2.572653000000
I	-1.096739000000	0.723876000000	-1.861704000000
Cu	-0.477194000000	1.032443000000	0.661868000000
N	-0.921115000000	3.462646000000	2.299068000000
N	-0.010410000000	2.948090000000	1.430111000000
N	-2.198492000000	1.593497000000	1.875543000000
N	-4.449839000000	1.339178000000	2.611794000000
C	1.084834000000	3.674439000000	1.562471000000
C	-2.153359000000	2.813892000000	2.403001000000
C	-3.268298000000	3.380769000000	3.026191000000
H	-3.266752000000	4.383137000000	3.418524000000
C	-0.391497000000	4.516027000000	3.014239000000
C	0.890960000000	4.665959000000	2.552532000000
H	1.609590000000	5.390760000000	2.905599000000
C	2.296828000000	3.393947000000	0.748805000000
H	2.084490000000	3.533022000000	-0.317228000000
H	3.119916000000	4.054903000000	1.032601000000
H	2.616085000000	2.356341000000	0.893059000000
C	-4.400444000000	2.582819000000	3.086065000000
H	-5.316223000000	2.959493000000	3.538544000000
C	-5.886404000000	-3.301028000000	0.549208000000
H	-5.524538000000	-4.006628000000	1.293107000000
C	-5.588826000000	-1.945268000000	0.690625000000
C	-1.062387000000	5.290521000000	4.093071000000
H	-1.530469000000	4.647821000000	4.846513000000
H	-0.304608000000	5.898892000000	4.593233000000
H	-1.819706000000	5.978810000000	3.701494000000
C	-6.653292000000	-3.752334000000	-0.523617000000
H	-6.903661000000	-4.804597000000	-0.613623000000
C	-3.335008000000	0.896071000000	2.032527000000
C	-6.799053000000	-1.498559000000	-1.359625000000
H	-7.138561000000	-0.792590000000	-2.111047000000
C	-6.031977000000	-1.051515000000	-0.290425000000
H	-5.771972000000	0.000582000000	-0.208896000000
C	-7.128002000000	-2.849733000000	-1.467081000000
H	-7.760259000000	-3.203360000000	-2.273182000000
S	-3.202426000000	-0.739685000000	1.438031000000
C	-4.815749000000	-1.462623000000	1.885017000000
H	-5.355573000000	-0.686803000000	2.436468000000

H	-4.612130000000	-2.287892000000	2.572762000000
First triplet excited state (T_1), **phase I**			
C	4.077727764010	-2.726184775537	-2.302947584095
C	3.619861896033	-3.636530704204	-1.370081041192
H	4.031286750588	-4.619667217767	-1.185496073790
C	2.535163626343	-3.038462562669	-0.710545437865
C	3.243275436249	-0.399664550609	-2.844788520923
C	4.074101285864	-0.068963979851	-3.920344089447
H	4.792046315037	-0.757995719304	-4.337944992842
C	3.934096062038	1.196713663075	-4.452508459349
H	4.545815489610	1.517034552801	-5.292049990549
C	2.297589569197	1.698809382631	-2.971090811013
C	1.385166037733	4.274552521805	-3.357892857669
H	2.432622945222	4.573926062423	-3.268776567255
H	1.206643885823	3.984003731494	-4.396014348221
C	0.453546152818	5.369615045423	-2.919639409811
C	0.797568726423	6.213146917046	-1.857824346608
H	1.747465373265	6.068532458838	-1.346821478554
C	-0.062266274958	7.230550292784	-1.451210501721
H	0.221598428836	7.880495632702	-0.627204974247
C	-1.281254237193	7.418059276701	-2.102800212315
H	-1.950193240858	8.216381577985	-1.790813324499
C	-1.634933746306	6.580804611441	-3.160006856068
H	-2.581941836800	6.721801084798	-3.675237098910
C	-0.773279342525	5.561835294388	-3.562246114349
H	-1.053257526239	4.907746073268	-4.385652412090
C	5.226443939329	-2.882846699958	-3.235091212667
H	4.919596293953	-2.891722886295	-4.288411176529
H	5.705336522417	-3.843640027125	-3.027367620796
H	5.984230660078	-2.100971111153	-3.103805549296
C	1.682746016734	-3.578309067488	0.378021005859
H	2.028137631151	-4.568036959947	0.687889682344
H	0.641745717278	-3.663897269681	0.048536550301
H	1.697228772523	-2.913309767275	1.248136721543
Cu	1.104580268576	-0.259264051487	-0.862888767925
I	1.427889649774	0.713492896933	1.603326158560
N	3.262006569871	-1.621839572786	-2.184625630886
N	2.329767715853	-1.821238746147	-1.211592439241
N	2.327167809819	0.492459478054	-2.372751487305
N	3.049356533607	2.104535051132	-3.979521076310
S	1.121192835790	2.809437427483	-2.295864985835
C	-4.077727764010	2.726184775537	2.302947584095
C	-3.619861896033	3.636530704204	1.370081041192
H	-4.031286750588	4.619667217767	1.185496073790
C	-2.535163626343	3.038462562669	0.710545437865
C	-3.243275436249	0.399664550609	2.844788520923
C	-4.074101285864	0.068963979851	3.920344089447
H	-4.792046315037	0.757995719304	4.337944992842
C	-3.934096062038	-1.196713663075	4.452508459349
H	-4.545815489610	-1.517034552801	5.292049990549
C	-2.297589569197	-1.698809382631	2.971090811013
C	-1.385166037733	-4.274552521805	3.357892857669
H	-2.432622945222	-4.573926062423	3.268776567255
H	-1.206643885823	-3.984003731494	4.396014348221

C	-0.453546152818	-5.369615045423	2.919639409811
C	-0.797568726423	-6.213146917046	1.857824346608
H	-1.747465373265	-6.068532458838	1.346821478554
C	0.062266274958	-7.230550292784	1.451210501721
H	-0.221598428836	-7.880495632702	0.627204974247
C	1.281254237193	-7.418059276701	2.102800212315
H	1.950193240858	-8.216381577985	1.790813324499
C	1.634933746306	-6.580804611441	3.160006856068
H	2.581941836800	-6.721801084798	3.675237098910
C	0.773279342525	-5.561835294388	3.562246114349
H	1.053257526239	-4.907746073268	4.385652412090
C	-5.226443939329	2.882846699958	3.235091212667
H	-4.919596293953	2.891722886295	4.288411176529
H	-5.705336522417	3.843640027125	3.027367620796
H	-5.984230660078	2.100971111153	3.103805549296
C	-1.682746016734	3.578309067488	-0.378021005859
H	-2.028137631151	4.568036959947	-0.687889682344
H	-0.641745717278	3.663897269681	-0.048536550301
H	-1.697228772523	2.913309767275	-1.248136721543
Cu	-1.104580268576	0.259264051487	0.862888767925
I	-1.427889649774	-0.713492896933	-1.603326158560
N	-3.262006569871	1.621839572786	2.184625630886
N	-2.329767715853	1.821238746147	1.211592439241
N	-2.327167809819	-0.492459478054	2.372751487305
N	-3.049356533607	-2.104535051132	3.979521076310
S	-1.121192835790	-2.809437427483	2.295864985835
First triplet excited state (T_1), **phase II**			
C	3.996394000000	-2.703289000000	-2.143930000000
C	3.780244000000	-3.481162000000	-1.024945000000
H	4.243276000000	-4.436140000000	-0.815874000000
C	2.856556000000	-2.793884000000	-0.218715000000
C	3.079160000000	-0.419260000000	-2.734683000000
C	3.716008000000	-0.183123000000	-3.955055000000
H	4.330898000000	-0.920479000000	-4.447979000000
C	3.523485000000	1.058791000000	-4.530712000000
H	3.983790000000	1.306676000000	-5.483595000000
C	2.196519000000	1.711827000000	-2.816670000000
C	1.344277000000	4.308972000000	-3.169859000000
H	2.394350000000	4.611087000000	-3.222424000000
H	1.049783000000	3.956237000000	-4.160817000000
C	0.463244000000	5.432987000000	-2.700465000000
C	0.785641000000	6.168027000000	-1.553534000000
H	1.682204000000	5.915905000000	-0.990569000000
C	-0.032212000000	7.210946000000	-1.125878000000
H	0.232122000000	7.771880000000	-0.232906000000
C	-1.184037000000	7.537401000000	-1.842224000000
H	-1.819523000000	8.355113000000	-1.511372000000
C	-1.513129000000	6.812265000000	-2.985863000000
H	-2.407345000000	7.061385000000	-3.552121000000
C	-0.696063000000	5.764602000000	-3.407615000000
H	-0.959222000000	5.197097000000	-4.298029000000
C	4.901609000000	-2.990651000000	-3.288505000000
H	4.363454000000	-3.065987000000	-4.241282000000
H	5.385378000000	-3.954433000000	-3.108225000000

H	5.692979000000	-2.239110000000	-3.398495000000
C	2.295809000000	-3.192281000000	1.097968000000
H	3.094263000000	-3.535937000000	1.764578000000
H	1.582990000000	-4.017436000000	0.988462000000
H	1.779733000000	-2.354606000000	1.573309000000
Cu	1.158596000000	-0.167954000000	-0.587223000000
I	1.167633000000	1.009411000000	1.752841000000
N	3.207554000000	-1.584579000000	-1.986141000000
N	2.515064000000	-1.652772000000	-0.813456000000
N	2.274160000000	0.528493000000	-2.175953000000
N	2.778914000000	2.032260000000	-3.957209000000
S	1.216269000000	2.913190000000	-1.995258000000
C	-3.996394000000	2.703289000000	2.143930000000
C	-3.780244000000	3.481162000000	1.024945000000
H	-4.243276000000	4.436140000000	0.815874000000
C	-2.856556000000	2.793884000000	0.218715000000
C	-3.079160000000	0.419260000000	2.734683000000
C	-3.716008000000	0.183123000000	3.955055000000
H	-4.330898000000	0.920479000000	4.447979000000
C	-3.523485000000	-1.058791000000	4.530712000000
H	-3.983790000000	-1.306676000000	5.483595000000
C	-2.196519000000	-1.711827000000	2.816670000000
C	-1.344277000000	-4.308972000000	3.169859000000
H	-2.394350000000	-4.611087000000	3.222424000000
H	-1.049783000000	-3.956237000000	4.160817000000
C	-0.463244000000	-5.432987000000	2.700465000000
C	-0.785641000000	-6.168027000000	1.553534000000
H	-1.682204000000	-5.915905000000	0.990569000000
C	0.032212000000	-7.210946000000	1.125878000000
H	-0.232122000000	-7.771880000000	0.232906000000
C	1.184037000000	-7.537401000000	1.842224000000
H	1.819523000000	-8.355113000000	1.511372000000
C	1.513129000000	-6.812265000000	2.985863000000
H	2.407345000000	-7.061385000000	3.552121000000
C	0.696063000000	-5.764602000000	3.407615000000
H	0.959222000000	-5.197097000000	4.298029000000
C	-4.901609000000	2.990651000000	3.288505000000
H	-4.363454000000	3.065987000000	4.241282000000
H	-5.385378000000	3.954433000000	3.108225000000
H	-5.692979000000	2.239110000000	3.398495000000
C	-2.295809000000	3.192281000000	-1.097968000000
H	-3.094263000000	3.535937000000	-1.764578000000
H	-1.582990000000	4.017436000000	-0.988462000000
H	-1.779733000000	2.354606000000	-1.573309000000
Cu	-1.158596000000	0.167954000000	0.587223000000
I	-1.167633000000	-1.009411000000	-1.752841000000
N	-3.207554000000	1.584579000000	1.986141000000
N	-2.515064000000	1.652772000000	0.813456000000
N	-2.274160000000	-0.528493000000	2.175953000000
N	-2.778914000000	-2.032260000000	3.957209000000
S	-1.216269000000	-2.913190000000	1.995258000000

Table S5. Optimized geometries of the **$[Cu_2(L^{Me})_2I_2]$** complex in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/Stuttgart RSC 1997/6-31+g(d) level of theory (ground state geometry - QM/MM model, triplet excited state geometry - gas phase).

Ground state (S_0)			
I	-0.060875000000	-0.041243000000	-2.267886000000
Cu	0.854369000000	1.032557000000	-0.049417000000
S	3.548496000000	-0.986252000000	-0.141185000000
N	2.173707000000	3.709826000000	-0.028659000000
N	2.985423000000	1.551360000000	-0.095953000000
N	5.308895000000	1.017547000000	-0.143377000000
N	0.946103000000	3.140277000000	-0.177213000000
C	4.018744000000	0.695770000000	-0.130984000000
C	4.603816000000	3.293566000000	-0.006766000000
H	4.864167000000	4.336285000000	0.062984000000
C	3.278919000000	2.848751000000	-0.037608000000
C	4.933067000000	-4.003833000000	1.086650000000
H	5.046804000000	-3.472717000000	2.027378000000
C	5.597930000000	2.322931000000	-0.079011000000
C	4.985074000000	-3.285038000000	-0.110392000000
C	3.182459000000	6.074202000000	0.126235000000
H	3.854235000000	5.859101000000	0.958572000000
H	2.747029000000	7.059617000000	0.308758000000
H	3.778887000000	6.138619000000	-0.790845000000
C	0.738837000000	5.370030000000	-0.122324000000
H	0.293216000000	6.355158000000	-0.129424000000
C	2.073775000000	5.088939000000	0.009000000000
C	4.614911000000	-6.064635000000	-0.128914000000
H	4.461846000000	-7.138856000000	-0.137558000000
C	0.074252000000	4.126523000000	-0.250745000000
C	4.838504000000	-3.977212000000	-1.315694000000
H	4.848452000000	-3.426925000000	-2.250875000000
C	5.184926000000	-1.795725000000	-0.101651000000
H	5.758634000000	-1.462234000000	-0.969973000000
H	5.714080000000	-1.469283000000	0.797840000000
C	4.748655000000	-5.384758000000	1.079731000000
H	4.718532000000	-5.932516000000	2.017176000000
C	7.052977000000	2.675135000000	-0.080724000000
H	7.509927000000	2.370537000000	0.865791000000
H	7.224019000000	3.745076000000	-0.222451000000
H	7.567169000000	2.118015000000	-0.868828000000
C	4.664265000000	-5.357901000000	-1.328706000000
H	4.566343000000	-5.880169000000	-2.276863000000
C	-1.370848000000	3.862686000000	-0.462435000000
H	-1.509949000000	2.859116000000	-0.872650000000
H	-1.796935000000	4.593226000000	-1.157139000000
H	-1.930735000000	3.935680000000	0.476976000000
I	0.060715000000	0.041270000000	2.267972000000
Cu	-0.854115000000	-1.032826000000	0.049532000000
S	-3.548410000000	0.986127000000	0.141201000000
N	-2.173656000000	-3.709939000000	0.028715000000
N	-2.985340000000	-1.551483000000	0.095950000000
N	-5.308800000000	-1.017676000000	0.143380000000
N	-0.946006000000	-3.140477000000	0.177253000000

C	-4.018654000000	-0.695881000000	0.130926000000
C	-4.603736000000	-3.293705000000	0.006802000000
H	-4.864088000000	-4.336417000000	-0.063014000000
C	-3.278840000000	-2.848867000000	0.037641000000
C	-4.933383000000	4.004111000000	-1.086397000000
H	-5.047448000000	3.473349000000	-2.027286000000
C	-5.597844000000	-2.323062000000	0.079088000000
C	-4.984961000000	3.284928000000	0.110393000000
C	-3.182572000000	-6.074307000000	-0.125750000000
H	-3.854420000000	-5.859381000000	-0.958084000000
H	-2.747175000000	-7.059774000000	-0.308064000000
H	-3.778945000000	-6.138482000000	0.791376000000
C	-0.738921000000	-5.370249000000	0.122567000000
H	-0.293324000000	-6.355385000000	0.129797000000
C	-2.073836000000	-5.089076000000	-0.008772000000
C	-4.614939000000	6.064552000000	0.129697000000
H	-4.462045000000	7.138781000000	0.138690000000
C	-0.074243000000	-4.126762000000	0.250842000000
C	-4.837990000000	3.976740000000	1.315894000000
H	-4.847551000000	3.426131000000	2.250862000000
C	-5.184830000000	1.795618000000	0.101345000000
H	-5.758849000000	1.461956000000	0.969394000000
H	-5.713648000000	1.469369000000	-0.798435000000
C	-4.748978000000	5.385060000000	-1.079109000000
H	-4.719141000000	5.933040000000	-2.016443000000
C	-7.052898000000	-2.675247000000	0.080979000000
H	-7.509864000000	-2.371153000000	-0.865682000000
H	-7.223975000000	-3.745111000000	0.223253000000
H	-7.567063000000	-2.117716000000	0.868805000000
C	-4.663886000000	5.357420000000	1.329300000000
H	-4.565756000000	5.879409000000	2.277590000000
C	1.370868000000	-3.863055000000	0.462580000000
H	1.510049000000	-2.859555000000	0.872955000000
H	1.796883000000	-4.593734000000	1.157183000000
H	1.930760000000	-3.935939000000	-0.476835000000
First triplet excited state (T_1)			
I	1.696227000000	-1.494782000000	0.101773000000
Cu	0.860512000000	0.932731000000	-0.651292000000
S	2.034999000000	2.408355000000	2.167540000000
N	2.208683000000	2.357517000000	-2.749416000000
N	2.229716000000	2.489033000000	-0.435058000000
N	3.598418000000	4.032444000000	0.765032000000
N	1.321820000000	1.339583000000	-2.565884000000
C	2.706983000000	3.062226000000	0.684084000000
C	3.675122000000	3.991713000000	-1.626665000000
H	4.088099000000	4.380451000000	-2.544891000000
C	2.720734000000	2.967251000000	-1.611759000000
C	1.384648000000	3.583045000000	5.410393000000
H	0.853875000000	4.381015000000	4.894807000000
C	4.092710000000	4.502085000000	-0.411194000000
C	2.477020000000	2.970647000000	4.787676000000
C	3.307689000000	3.600736000000	-4.701238000000
H	3.028463000000	4.621660000000	-4.413493000000
H	3.216995000000	3.529753000000	-5.788669000000

H	4.364936000000	3.449327000000	-4.450250000000
C	1.633398000000	1.646584000000	-4.754463000000
H	1.552636000000	1.530864000000	-5.826895000000
C	2.419884000000	2.572351000000	-4.094832000000
C	1.647182000000	2.156925000000	7.341928000000
H	1.330023000000	1.846432000000	8.334474000000
C	0.965906000000	0.899965000000	-3.772304000000
C	3.144028000000	1.940619000000	5.458819000000
H	3.990851000000	1.452055000000	4.980830000000
C	2.920266000000	3.404970000000	3.418708000000
H	3.993750000000	3.258451000000	3.275603000000
H	2.698354000000	4.459545000000	3.237370000000
C	0.972179000000	3.181476000000	6.679153000000
H	0.124535000000	3.671760000000	7.151607000000
C	5.107640000000	5.593831000000	-0.307613000000
H	4.684845000000	6.455466000000	0.223637000000
H	5.455640000000	5.922842000000	-1.291326000000
H	5.971743000000	5.254296000000	0.276818000000
C	2.734659000000	1.536541000000	6.727693000000
H	3.267616000000	0.738099000000	7.238137000000
C	-0.001512000000	-0.214771000000	-3.927455000000
H	0.357656000000	-1.113164000000	-3.413997000000
H	-0.155098000000	-0.453924000000	-4.983016000000
H	-0.968679000000	0.048239000000	-3.485247000000
I	-1.696227000000	1.494782000000	-0.101773000000
Cu	-0.860512000000	-0.932731000000	0.651292000000
S	-2.034999000000	-2.408355000000	-2.167540000000
N	-2.208683000000	-2.357517000000	2.749416000000
N	-2.229716000000	-2.489033000000	0.435058000000
N	-3.598418000000	-4.032444000000	-0.765032000000
N	-1.321820000000	-1.339583000000	2.565884000000
C	-2.706983000000	-3.062226000000	-0.684084000000
C	-3.675122000000	-3.991713000000	1.626665000000
H	-4.088099000000	-4.380451000000	2.544891000000
C	-2.720734000000	-2.967251000000	1.611759000000
C	-1.384648000000	-3.583045000000	-5.410393000000
H	-0.853875000000	-4.381015000000	-4.894807000000
C	-4.092710000000	-4.502085000000	0.411194000000
C	-2.477020000000	-2.970647000000	-4.787676000000
C	-3.307689000000	-3.600736000000	4.701238000000
H	-3.028463000000	-4.621660000000	4.413493000000
H	-3.216995000000	-3.529753000000	5.788669000000
H	-4.364936000000	-3.449327000000	4.450250000000
C	-1.633398000000	-1.646584000000	4.754463000000
H	-1.552636000000	-1.530864000000	5.826895000000
C	-2.419884000000	-2.572351000000	4.094832000000
C	-1.647182000000	-2.156925000000	-7.341928000000
H	-1.330023000000	-1.846432000000	-8.334474000000
C	-0.965906000000	-0.899965000000	3.772304000000
C	-3.144028000000	-1.940619000000	-5.458819000000
H	-3.990851000000	-1.452055000000	-4.980830000000
C	-2.920266000000	-3.404970000000	-3.418708000000
H	-3.993750000000	-3.258451000000	-3.275603000000
H	-2.698354000000	-4.459545000000	-3.237370000000

C	-0.972179000000	-3.181476000000	-6.679153000000
H	-0.124535000000	-3.671760000000	-7.151607000000
C	-5.107640000000	-5.593831000000	0.307613000000
H	-4.684845000000	-6.455466000000	-0.223637000000
H	-5.455640000000	-5.922842000000	1.291326000000
H	-5.971743000000	-5.254296000000	-0.276818000000
C	-2.734659000000	-1.536541000000	-6.727693000000
H	-3.267616000000	-0.738099000000	-7.238137000000
C	0.001512000000	0.214771000000	3.927455000000
H	-0.357656000000	1.113164000000	3.413997000000
H	0.155098000000	0.453924000000	4.983016000000
H	0.968679000000	-0.048239000000	3.485247000000

Table S6. Optimized geometries of the **$[Cu_2(L^H)_2Br_2]$** complex in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/Stuttgart RSC 1997/6-31+g(d) level of theory (ground state geometry - QM/MM model, triplet excited state geometry - gas phase).

Ground state (S_0)			
Br	-2.494671000000	0.028480000000	2.123103000000
Cu	-1.492296000000	-1.396626000000	0.399247000000
S	-4.252285000000	-3.304774000000	0.487492000000
N	0.607250000000	-3.426983000000	0.054999000000
N	-1.686747000000	-3.538874000000	0.265576000000
N	-2.903432000000	-5.595147000000	0.223033000000
N	0.492846000000	-2.108341000000	0.364590000000
C	-6.820603000000	-3.897868000000	0.863635000000
C	-8.245695000000	-2.876666000000	2.529584000000
H	-8.448712000000	-2.675115000000	3.575168000000
C	-9.157424000000	-2.505878000000	1.541031000000
H	-10.066885000000	-1.973833000000	1.807613000000
C	-7.077292000000	-3.549085000000	2.192006000000
H	-6.362830000000	-3.820157000000	2.966042000000
C	-8.901910000000	-2.838190000000	0.212314000000
H	-9.603746000000	-2.555645000000	-0.568722000000
C	-0.543933000000	-4.206757000000	0.135836000000
C	-7.745587000000	-3.541173000000	-0.117840000000
H	-7.549144000000	-3.817100000000	-1.148458000000
C	-1.741191000000	-6.242187000000	0.132562000000
H	-1.797860000000	-7.328632000000	0.091742000000
C	1.691888000000	-1.579643000000	0.213437000000
C	1.898449000000	-3.743139000000	-0.317803000000
C	-2.814120000000	-4.267560000000	0.310511000000
C	2.603871000000	-2.573880000000	-0.220330000000
H	3.648366000000	-2.459310000000	-0.459343000000
C	-0.514779000000	-5.601181000000	0.101331000000
H	0.412759000000	-6.142891000000	0.078031000000
C	-5.541138000000	-4.593755000000	0.503002000000
H	-5.595885000000	-5.071703000000	-0.479158000000
H	-5.263085000000	-5.354188000000	1.237508000000
C	2.401519000000	-5.066412000000	-0.780481000000
H	2.505827000000	-5.790442000000	0.036486000000
H	3.394997000000	-4.922764000000	-1.213989000000
H	1.759906000000	-5.503415000000	-1.551444000000

C	1.933291000000	-0.144168000000	0.505073000000
H	1.018473000000	0.319583000000	0.881952000000
H	2.253710000000	0.392712000000	-0.394210000000
H	2.721180000000	-0.029356000000	1.256931000000
Br	-1.804865000000	-0.418609000000	-1.925245000000
Cu	-2.807640000000	1.006334000000	-0.201415000000
S	-0.047923000000	2.914297000000	-0.289331000000
N	-4.907399000000	3.036488000000	0.143181000000
N	-2.613464000000	3.148419000000	-0.067612000000
N	-1.396753000000	5.204697000000	-0.025114000000
N	-4.792899000000	1.717840000000	-0.166367000000
C	2.520321000000	3.507191000000	-0.665899000000
C	3.945019000000	2.485978000000	-2.332190000000
H	4.147836000000	2.284608000000	-3.377837000000
C	4.856878000000	2.115012000000	-1.343831000000
H	5.766231000000	1.582866000000	-1.610584000000
C	2.776749000000	3.158498000000	-1.994341000000
H	2.062221000000	3.429753000000	-2.768253000000
C	4.601628000000	2.447243000000	-0.015037000000
H	5.303629000000	2.164608000000	0.765821000000
C	-3.756265000000	3.816345000000	0.062095000000
C	3.445450000000	3.150327000000	0.315390000000
H	3.249232000000	3.426178000000	1.346071000000
C	-2.558994000000	5.851770000000	0.065047000000
H	-2.502320000000	6.938222000000	0.105723000000
C	-5.991925000000	1.189073000000	-0.015271000000
C	-6.198637000000	3.352562000000	0.515942000000
C	-1.486083000000	3.877107000000	-0.112590000000
C	-6.903976000000	2.183256000000	0.418475000000
H	-7.948451000000	2.068494000000	0.657521000000
C	-3.785427000000	5.210773000000	0.096281000000
H	-4.712968000000	5.752496000000	0.119239000000
C	1.241004000000	4.203214000000	-0.304996000000
H	1.295988000000	4.681117000000	0.677162000000
H	0.962898000000	4.963672000000	-1.039441000000
C	-6.701667000000	4.675820000000	0.978700000000
H	-6.806074000000	5.399857000000	0.161754000000
H	-7.695100000000	4.532188000000	1.412315000000
H	-6.059953000000	5.112796000000	1.749594000000
C	-6.233205000000	-0.246410000000	-0.306983000000
H	-5.318407000000	-0.709988000000	-0.684128000000
H	-6.553349000000	-0.783407000000	0.592306000000
H	-7.021267000000	-0.361224000000	-1.058673000000
First triplet excited state (T_1)			
Br	-0.881970000000	0.713520000000	-1.443462000000
Cu	-1.425642000000	-0.366491000000	0.730142000000
S	-2.126502000000	-2.939628000000	-1.273541000000
N	-3.809486000000	0.029361000000	2.282405000000
N	-3.173599000000	-1.423633000000	0.583725000000
N	-4.568796000000	-3.175702000000	-0.241251000000
N	-2.523663000000	0.478131000000	2.230586000000
C	-1.803998000000	-5.005121000000	-3.004042000000
C	-0.883359000000	-5.216340000000	-5.238863000000
H	-0.921383000000	-4.962283000000	-6.295438000000

C	0.103724000000	-6.076819000000	-4.760797000000
H	0.838368000000	-6.498290000000	-5.442571000000
C	-1.828191000000	-4.682657000000	-4.364337000000
H	-2.596592000000	-4.009839000000	-4.739936000000
C	0.140963000000	-6.399232000000	-3.404339000000
H	0.906514000000	-7.071052000000	-3.023957000000
C	-4.148376000000	-1.041176000000	1.457139000000
C	-0.806154000000	-5.865578000000	-2.533555000000
H	-0.774447000000	-6.117864000000	-1.475381000000
C	-5.528518000000	-2.779921000000	0.627180000000
H	-6.453667000000	-3.350180000000	0.610548000000
C	-2.422559000000	1.484971000000	3.095854000000
C	-4.540311000000	0.763309000000	3.191584000000
C	-3.446468000000	-2.482044000000	-0.207384000000
C	-3.664572000000	1.690894000000	3.721228000000
H	-3.905124000000	2.436320000000	4.467464000000
C	-5.365863000000	-1.723480000000	1.505171000000
H	-6.152796000000	-1.467453000000	2.198340000000
C	-2.826375000000	-4.433196000000	-2.062238000000
H	-3.093124000000	-5.143763000000	-1.275433000000
H	-3.743764000000	-4.151075000000	-2.584482000000
C	-5.984984000000	0.594209000000	3.504553000000
H	-6.615798000000	0.652910000000	2.609482000000
H	-6.287315000000	1.402359000000	4.176185000000
H	-6.201096000000	-0.352901000000	4.014943000000
C	-1.147419000000	2.232264000000	3.265891000000
H	-0.286419000000	1.573709000000	3.119817000000
H	-1.089327000000	2.680678000000	4.261764000000
H	-1.069503000000	3.044210000000	2.532283000000
Br	0.881970000000	-0.713520000000	1.443462000000
Cu	1.425642000000	0.366491000000	-0.730142000000
S	2.126502000000	2.939628000000	1.273541000000
N	3.809486000000	-0.029361000000	-2.282405000000
N	3.173599000000	1.423633000000	-0.583725000000
N	4.568796000000	3.175702000000	0.241251000000
N	2.523663000000	-0.478131000000	-2.230586000000
C	1.803998000000	5.005121000000	3.004042000000
C	0.883359000000	5.216340000000	5.238863000000
H	0.921383000000	4.962283000000	6.295438000000
C	-0.103724000000	6.076819000000	4.760797000000
H	-0.838368000000	6.498290000000	5.442571000000
C	1.828191000000	4.682657000000	4.364337000000
H	2.596592000000	4.009839000000	4.739936000000
C	-0.140963000000	6.399232000000	3.404339000000
H	-0.906514000000	7.071052000000	3.023957000000
C	4.148376000000	1.041176000000	-1.457139000000
C	0.806154000000	5.865578000000	2.533555000000
H	0.774447000000	6.117864000000	1.475381000000
C	5.528518000000	2.779921000000	-0.627180000000
H	6.453667000000	3.350180000000	-0.610548000000
C	2.422559000000	-1.484971000000	-3.095854000000
C	4.540311000000	-0.763309000000	-3.191584000000
C	3.446468000000	2.482044000000	0.207384000000
C	3.664572000000	-1.690894000000	-3.721228000000

H	3.905124000000	-2.436320000000	-4.467464000000
C	5.365863000000	1.723480000000	-1.505171000000
H	6.152796000000	1.467453000000	-2.198340000000
C	2.826375000000	4.433196000000	2.062238000000
H	3.093124000000	5.143763000000	1.275433000000
H	3.743764000000	4.151075000000	2.584482000000
C	5.984984000000	-0.594209000000	-3.504553000000
H	6.615798000000	-0.652910000000	-2.609482000000
H	6.287315000000	-1.402359000000	-4.176185000000
H	6.201096000000	0.352901000000	-4.014943000000
C	1.147419000000	-2.232264000000	-3.265891000000
H	0.286419000000	-1.573709000000	-3.119817000000
H	1.089327000000	-2.680678000000	-4.261764000000
H	1.069503000000	-3.044210000000	-2.532283000000

References

[1] N. J. Basha, C. U. Reddy and N. M. Goudgaon, Cyclization of 4-(2-aminoanilino)-2-benzylthiopyrimidine to novel 1-(2-benzylthiopyrimidin-4-yl)-2-substituted benzimidazoles, *Heterocycl. Commun.*, 2008, **14**, 469-472. https://doi.org/10.1515/HC.2008.14.6.469

[2] A. V. Erkin, V. I. Krutikov and E. B. Smirnova, Synthesis and Antimicobacterial Activity of 2-Substituted 4-Arylamino-6-methylpyrimidines, *Russ. J. Gen. Chem.*, 2008, **78**, 1944-1948. https://doi.org/10.1134/s1070363208100216

[3] K. A. Vinogradova, V. F. Plyusnin, A. S. Kupryakov, M. I. Rakhmanova, N. V. Pervukhina, D. Y. Naumov, L. A. Sheludyakova, E. B. Nikolaenkova, V. P. Krivopalov and M. B. Bushuev, Halide impact on emission of mononuclear copper(I) complexes with pyrazolylpyrimidine and triphenylphosphine, *Dalton Trans.*, 2014, **43**, 2953-2960. https://doi.org/10.1039/C3DT53040J

[4] N. A. Shekhovtsov, T. E. Kokina, K. A. Vinogradova, A. Y. Panarin, M. I. Rakhmanova, D. Y. Naumov, N. V. Pervukhina, E. B. Nikolaenkova, V. P. Krivopalov, R. Czerwieniec and M. B. Bushuev, Near-infrared emitting copper(I) complexes with a pyrazolylpyrimidine ligand: exploring relaxation pathways, *Dalton Trans.*, 2022, **51**, 2898-2911. https://doi.org/10.1039/D1DT04325K

[5] K. A. Vinogradova, V. P. Krivopalov, E. B. Nikolaenkova, N. V. Pervukhina, D. Y. Naumov, L. A. Sheludyakova and M. B. Bushuev, Copper(II) and copper(I) tetrafluoroborate complexes with 4-(3,5-diphenyl-1*H*-pyrazol-1-yl)-6-(piperidin-1-yl)pyrimidine (L): Synthesis, structures and luminescence, *Inorg. Chim. Acta*, 2012, **386**, 116-121. https://doi.org/10.1016/j.ica.2012.02.004

[6] K. A. Vinogradova, V. P. Krivopalov, E. B. Nikolaenkova, N. V. Pervukhina, D. Y. Naumov, M. I. Rakhmanova, E. G. Boguslavsky, L. A. Sheludyakova and M. B. Bushuev, Synthesis and structures of copper(II), copper(I,II) and copper(I) complexes with 4-(3,5-diphenyl-1*H*-pyrazol-1-yl)-6-(piperidin-1-yl)pyrimidine. Luminescence of copper(I) complexes, *Polyhedron*, 2013, **57**, 1-13. https://doi.org/10.1016/j.poly.2013.04.009

[7] Bruker Apex3 software suite: Apex3, SADABS-2016/2 and SAINT 8.40a; Publisher: Bruker AXS Inc., Madison, WI, USA, 2017.

[8] G. M. Sheldrick, SHELXT – Integrated space-group and crystal-structure determination, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3–8. https://doi.org/10.1107/S2053273314026370

[9] G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8, https://doi.org/10.1107/S2053229614024218

[10] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.*, 2009, **42**, 339–341, https://doi.org/10.1107/S0021889808042726