

Supporting Information

Structural and luminescence properties of Cu(I)X-Quinoxaline under High Pressure (X=Br, I)

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Experimental Section

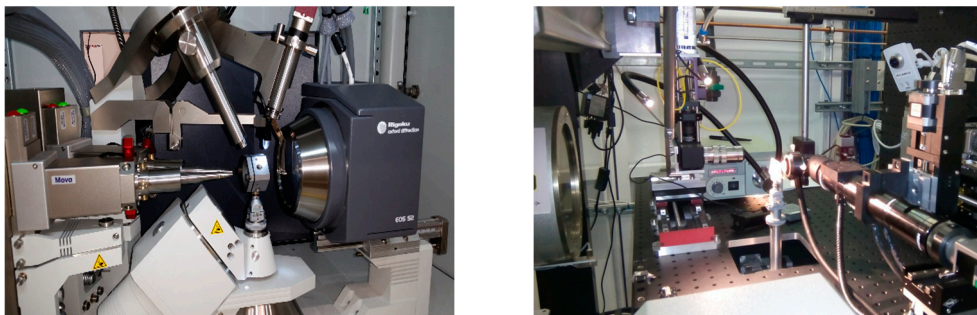


Figure S1. Instrumental setup used for HP experiments. On the left, a SuperNOVA diffractometer with EoS CCD detector. On the right, HP Station in MSPD-BL04 (ALBA Synchrotron) with Rayonix SX165 CCD Detector.



Figure S2. Bragg-Mini DAC (Almax EasyLab company) with 500 μ m diameter in the culets of diamonds (top). Paderborn Mini DAC with 400 μ m diameter in the culets of diamonds (bottom)

Crystal Data

Table S1-1. Crystal data and structure refinements for (CuBr)₂-Quin sample at different pressures (0.00-4.67GPa) at room temperature.

	0.00 GPa	0.22 GPa	0.72GPa	1.17 GPa
CCDC	2226261	2226239	2226259	2226258
Formula	C ₈ H ₆ N ₂ Cu ₂ Br ₂	C ₈ H ₆ Br ₂ Cu ₂ N ₂	C ₈ H ₆ Br ₂ Cu ₂ N ₂	C ₈ H ₆ Br ₂ Cu ₂ N ₂
$D_{calc}/\text{g cm}^{-3}$	2.806	2.842	2.926	2.993
μ/mm^{-1}	12.355	12.517	12.886	13.179
Formula Weight	417.05	417.05	417.05	417.05
Colour	brown	brown	brown	brown
Shape	plate-shaped	plate-shaped	plate-shaped	plate-shaped
Size/mm ³	0.14×0.05×0.03	0.14×0.05×0.04	0.14×0.05×0.04	0.14×0.05×0.04
T/K	293(2)	293(2)	293(2)	293(2)
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
$a/\text{\AA}$	4.1080(2)	4.1001(7)	4.0748(3)	4.0582(5)
$b/\text{\AA}$	17.6594(7)	17.631(3)	17.4994(16)	17.416(2)
$c/\text{\AA}$	13.6139(9)	13.49(3)	13.284(17)	13.11(2)
$\alpha/^\circ$	90	90	90	90
$\beta/^\circ$	91.496(6)	91.79(4)	92.17(2)	92.75(3)
$\gamma/^\circ$	90	90	90	90
$V/\text{\AA}^3$	987.28(9)	975(2)	946.6(12)	925.5(14)
Z	4	4	4	4
Z'	1	1	1	1
Wavelength/ \AA	0.71073	0.71073	0.71073	0.71073
Radiation type	Mo K_α	Mo K_α	Mo K_α	Mo K_α
$\theta_{min}/^\circ$	1.889	2.310	2.328	2.339
$\theta_{max}/^\circ$	29.163	26.345	26.355	26.370
Measured Refl.	4422	1856	2418	1950
Indep't Refl's	1974	670	651	637
Refl's $I \geq 2 \sigma(I)$	1629	478	530	525
R_{int}	0.0236	0.0560	0.0321	0.0301
Parameters	127	77	77	77
Restraints	0	0	0	0
Largest Peak	0.658	0.565	0.350	0.429
Deepest Hole	-0.798	-0.527	-0.406	-0.387
GooF	1.138	1.127	1.233	1.222
wR_2 (all data)	0.0699	0.1688	0.0824	0.1070
wR_2	0.0656	0.1428	0.0751	0.1002
R_1 (all data)	0.0529	0.0941	0.0471	0.0557
R_1	0.0386	0.0604	0.0347	0.0433

Table S1-2. Crystal data and structure refinements for (CuBr)₂-Quin sample at different pressures (0.00-4.67GPa) at room temperature.

	1.54 GPa	1.92 GPa	2.16GPa	2.54 GPa
CCDC	2226251	2226252	2226262	2226243
Formula	C ₈ H ₆ Br ₂ Cu ₂ N ₂	C ₈ H ₆ Br ₂ Cu ₂ N ₂	C ₈ H ₆ Br ₂ Cu ₂ N ₂	C ₈ H ₆ Br ₂ Cu ₂ N ₂
<i>D</i> _{calc.} / g cm ⁻³	3.038	3.077	3.104	3.141
μ /mm ⁻¹	13.377	13.549	13.670	13.830
Formula Weight	417.05	417.05	417.05	417.05
Colour	brown	brown	brown	brown
Shape	plate-shaped	plate-shaped	plate-shaped	plate-shaped
Size/mm ³	0.14×0.05×0.04	0.14×0.05×0.04	0.14×0.05×0.04	0.14×0.05×0.04
<i>T</i> /K	293(2)	293(2)	293(2)	293(2)
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	4.0491(5)	4.0427(4)	4.0458(4)	4.0217(6)
<i>b</i> /Å	17.356(2)	17.2708(17)	17.2700(18)	17.112(3)
<i>c</i> /Å	12.994(19)	12.915(15)	12.794(14)	12.84(2)
α /°	90	90	90	90
β /°	93.14(3)	93.24(2)	93.40(2)	93.67(4)
γ /°	90	90	90	90
<i>V</i> /Å ³	911.8(14)	900.3(10)	892.3(10)	882.0(15)
<i>Z</i>	4	4	4	4
<i>Z</i> '	1	1	1	1
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Radiation type	Mo K α	Mo K α	Mo K α	Mo K α
θ _{min} /°	2.347	2.359	2.359	2.380
θ _{max} /°	26.370	26.349	26.348	26.358
Measured Refl.	1932	1816	2061	1595
Indep't Refl's	628	623	618	629
Refl's I≥2 σ (I)	496	510	490	446
<i>R</i> _{int}	0.0373	0.0269	0.0382	0.0457
Parameters	77	77	77	77
Restraints	0	0	0	0
Largest Peak	0.571	0.428	0.698	0.701
Deepest Hole	-0.585	-0.461	-0.729	-0.707
GooF	1.228	1.245	1.209	1.151
<i>wR</i> ₂ (all data)	0.1293	0.1173	0.1744	0.1592
<i>wR</i> ₂	0.1142	0.1094	0.1593	0.1293
<i>R</i> ₁ (all data)	0.0696	0.0536	0.0759	0.0941
<i>R</i> ₁	0.0489	0.0405	0.0587	0.0573

Table S1-3. Crystal data and structure refinements for (CuBr)₂-Quin sample at different pressures (0.00-4.67GPa) at room temperature.

	3.16 GPa	3.56 GPa	3.97GPa	4.62 GPa
CCDC	2226240	2226244	2226257	2226264
Formula	C ₈ H ₆ Br ₂ Cu ₂ N ₂	C ₈ H ₆ Cu ₂ Br ₂ N ₂	C ₈ H ₆ Cu ₂ Br ₂ N ₂	C ₈ H ₆ Br ₂ Cu ₂ N ₂
<i>D</i> _{calc.} / g cm ⁻³	3.205	3.245	3.276	3.319
μ /mm ⁻¹	14.114	14.291	14.424	14.616
Formula Weight	417.05	417.05	417.05	417.05
Colour	brown	brown	brown	brown
Shape	plate-shaped	plate-shaped	plate-shaped	plate-shaped
Size/mm ³	0.14×0.05×0.04	0.14×0.05×0.04	0.11×0.05×0.04	0.14×0.05×0.04
<i>T</i> /K	293(2)	298(2)	298(2)	298(2)
Crystal System	monoclinic	triclinic	triclinic	triclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	4.0403(3)	4.0457(9)	4.0608(10)	4.0605(12)
<i>b</i> /Å	17.0981(12)	17.0296(16)	16.9204(19)	16.839(3)
<i>c</i> /Å	12.544(9)	12.438(5)	12.376(5)	12.287(7)
α /°	90	88.73(2)	88.34(2)	88.48(3)
β /°	94.18(2)	94.39(4)	94.54(4)	94.88(5)
γ /°	90	87.861(13)	86.499(15)	86.038(18)
<i>V</i> /Å ³	864.2(6)	853.6(4)	845.7(4)	834.6(6)
<i>Z</i>	4	4	4	4
<i>Z</i> '	1	2	2	2
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Radiation type	Mo K α	Mo K α	Mo K α	Mo K α
θ_{min} /°	2.382	2.394	2.413	2.426
θ_{max} /°	26.352	23.251	23.256	23.231
Measured Refl.	1536	2820	2174	2350
Indep't Refl's	507	841	871	883
Refl's $I \geq 2 \sigma(I)$	412	582	586	558
<i>R</i> _{int}	0.0288	0.0664	0.0608	0.0933
Parameters	77	87	87	87
Restraints	0	14	14	14
Largest Peak	0.502	1.426	1.177	1.712
Deepest Hole	-0.410	-1.130	-1.156	-1.121
GooF	1.193	1.119	1.170	1.156
<i>wR</i> ₂ (all data)	0.1059	0.3595	0.3637	0.4130
<i>wR</i> ₂	0.0971	0.3205	0.3176	0.3665
<i>R</i> ₁ (all data)	0.0563	0.1887	0.1889	0.2170
<i>R</i> ₁	0.0422	0.1375	0.1372	0.1575

Table S2-1. Crystal data and structure refinements for (CuI)₂-Quin sample at different pressures (0.00-7.00GPa) at room temperature.

	0.00 GPa	0.47 GPa	0.90GPa	1.36 GPa
CCDC	2226248	2226249	2226241	2226254
Formula	C ₈ H ₆ Cu ₂ I ₂ N ₂	C ₈ H ₆ Cu ₂ I ₂ N ₂	C ₈ H ₆ Cu ₂ I ₂ N ₂	C ₈ H ₆ Cu ₂ I ₂ N ₂
<i>D</i> _{calc.} / g cm ⁻³	3.165	3.267	3.348	3.423
μ /mm ⁻¹	9.680	9.992	10.241	10.470
Formula Weight	511.03	511.03	511.03	511.03
Colour	yellow	brown	brown	brown
Shape	plate-shaped	plate-shaped	plate-shaped	plate-shaped
Size/mm ³	0.07×0.03×0.01	0.07×0.03×0.01	0.07×0.03×0.01	0.07×0.03×0.01
<i>T</i> /K	298(1)	298(2)	298(2)	298(2)
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	4.3719(2)	4.35209(15)	4.34081(14)	4.33064(15)
<i>b</i> /Å	17.7203(8)	17.5879(7)	17.4953(6)	17.3971(7)
<i>c</i> /Å	13.8614(6)	13.599(6)	13.380(5)	13.198(6)
α /°	90	90	90	90
β /°	92.886(4)	93.523(8)	93.899(8)	94.268(9)
γ /°	90	90	90	90
<i>V</i> /Å ³	1072.50(8)	1039.0(5)	1013.8(4)	991.6(4)
<i>Z</i>	4	4	4	4
<i>Z</i> '	1	1	1	1
Wavelength/Å	0.71073	0.3185	0.3185	0.3185
Radiation type	MoK α	synchrotron	synchrotron	synchrotron
θ _{min} /°	1.867	2.076	2.087	2.098
θ _{max} /°	26.370	11.478	11.478	11.478
Measured Refl.	4012	1657	1647	1605
Indep't Refl's	2198	857	841	826
Refl's I≥2 σ (I)	1838	714	714	695
<i>R</i> _{int}	0.0289	0.0455	0.0386	0.0384
Parameters	127	77	77	77
Restraints	0	0	0	0
Largest Peak	0.742	1.145	1.100	0.818
Deepest Hole	-0.798	-1.147	-1.473	-0.739
GooF	1.055	1.045	1.034	1.087
<i>wR</i> ₂ (all data)	0.0681	0.1752	0.1591	0.1386
<i>wR</i> ₂	0.0638	0.1650	0.1520	0.1295
<i>R</i> ₁ (all data)	0.0516	0.0743	0.0667	0.0584
<i>R</i> ₁	0.0376	0.0649	0.0593	0.0497

Table S2-2. Crystal data and structure refinements for (CuI)₂-Quin sample at different pressures (0.00-7.00GPa) at room temperature.

	1.80 GPa	2.20 GPa	2.64GPa	3.25 GPa
CCDC	2226263	2226245	2226247	2226256
Formula	C ₈ H ₆ Cu ₂ I ₂ N ₂	C ₈ H ₆ Cu ₂ I ₂ N ₂	C ₈ H ₆ Cu ₂ I ₂ N ₂	C ₈ H ₆ Cu ₂ I ₂ N ₂
$D_{calc.}/\text{g cm}^{-3}$	3.490	3.540	3.595	3.667
μ/mm^{-1}	10.673	10.826	10.995	11.215
Formula Weight	511.03	511.03	511.03	511.03
Colour	brown	brown	brown	brown
Shape	plate-shaped	plate-shaped	plate-shaped	plate-shaped
Size/mm ³	0.07×0.03×0.01	0.07×0.03×0.01	0.07×0.03×0.01	0.07×0.03×0.01
T/K	298(2)	298(2)	298(2)	298(2)
Crystal System	monoclinic	monoclinic	monoclinic	triclinic
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P-1$
$a/\text{\AA}$	4.32447(14)	4.31914(15)	4.31385(15)	4.3090(2)
$b/\text{\AA}$	17.3162(6)	17.2490(7)	17.1743(6)	17.0807(9)
$c/\text{\AA}$	13.030(5)	12.916(5)	12.794(5)	12.645(2)
$\alpha/^\circ$	90	90	90	88.916(11)
$\beta/^\circ$	94.505(8)	94.749(9)	94.988(9)	95.228(11)
$\gamma/^\circ$	90	90	90	92.637(4)
$V/\text{\AA}^3$	972.7(4)	959.0(4)	944.2(4)	925.71(17)
Z	4	4	4	4
Z'	1	1	1	2
Wavelength/ \AA	0.3185	0.3185	0.3185	0.3185
Radiation type	synchrotron	synchrotron	synchrotron	synchrotron
$\theta_{min}/^\circ$	2.108	2.116	2.126	2.129
$\theta_{max}/^\circ$	11.481	11.479	11.476	11.779
Measured Refl.	1585	1619	1490	1584
Indep't Refl's	811	811	786	1242
Refl's $I \geq 2\sigma(I)$	686	669	648	796
R_{int}	0.0363	0.0348	0.0520	0.0476
Parameters	72	77	77	99
Restraints	0	0	0	12
Largest Peak	2.490	1.379	1.088	1.512
Deepest Hole	-2.566	-1.200	-0.892	-1.487
GooF	1.043	1.078	1.020	1.057
wR_2 (all data)	0.1985	0.1764	0.1432	0.3065
wR_2	0.1857	0.1654	0.1358	0.2681
R_1 (all data)	0.0789	0.0679	0.0641	0.1360
R_1	0.0703	0.0584	0.0558	0.0976

Table S2-3. Crystal data and structure refinements for (CuI)₂-Quin sample at different pressures (0.00-7.00GPa) at room temperature.

	3.69 GPa	4.20 GPa	4.81GPa	5.43 GPa
CCDC	2226253	2226250	2226246	2226260
Formula	C ₈ H ₆ Cu ₂ I ₂ N ₂	C ₈ H ₆ Cu ₂ I ₂ N ₂	C ₈ H ₆ Cu ₂ I ₂ N ₂	C ₈ H ₆ Cu ₂ I ₂ N ₂
$D_{calc.}/\text{g cm}^{-3}$	3.712	3.768	3.821	3.878
μ/mm^{-1}	11.354	11.524	11.687	11.863
Formula Weight	511.03	511.03	511.03	511.03
Colour	brown	brown	brown	brown
Shape	plate-shaped	plate-shaped	plate-shaped	plate-shaped
Size/mm ³	0.07×0.03×0.01	0.07×0.03×0.01	0.07×0.03×0.01	0.07×0.03×0.01
T/K	298(2)	298(2)	298(2)	298(2)
Crystal System	triclinic	triclinic	triclinic	triclinic
Space Group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
$a/\text{\AA}$	4.3058(2)	4.2967(2)	4.2856(2)	4.2732(2)
$b/\text{\AA}$	17.0097(8)	16.9316(9)	16.8529(8)	16.7757(8)
$c/\text{\AA}$	12.575(2)	12.4932(16)	12.4245(18)	12.3479(15)
$\alpha/^\circ$	87.899(9)	87.230(10)	86.825(9)	86.492(9)
$\beta/^\circ$	95.572(9)	95.864(10)	96.157(10)	96.410(9)
$\gamma/^\circ$	93.641(4)	94.214(5)	94.615(4)	94.934(4)
$V/\text{\AA}^3$	914.40(16)	900.93(14)	888.30(14)	875.19(12)
Z	4	4	4	4
Z'	2	2	2	2
Wavelength/ \AA	0.3185	0.3185	0.3185	0.3185
Radiation type	synchrotron	synchrotron	synchrotron	synchrotron
$\theta_{min}/^\circ$	2.134	2.140	2.148	2.156
$\theta_{max}/^\circ$	11.778	11.781	11.777	11.778
Measured Refl.	1581	1583	1463	1524
Indep't Refl's	1232	1222	1165	1188
Refl's $I \geq 2\sigma(I)$	812	798	780	779
R_{int}	0.0354	0.0273	0.0193	0.0228
Parameters	75	75	75	75
Restraints	0	0	0	0
Largest Peak	1.987	2.408	1.611	2.052
Deepest Hole	-1.606	-1.863	-1.574	-1.589
GooF	1.047	1.022	1.070	1.088
wR_2 (all data)	0.2599	0.2657	0.2302	0.2245
wR_2	0.2219	0.2335	0.2040	0.2019
R_1 (all data)	0.1148	0.1155	0.0982	0.0982
R_1	0.0815	0.0871	0.0728	0.0706

Table S2-4. Crystal data and structure refinements for (CuI)₂-Quin sample at different pressures (0.00-7.00GPa) at room temperature.

	6.21 GPa	7.00 GPa
CCDC	2226255	2226242
Formula	C ₈ H ₆ Cu ₂ I ₂ N ₂	C ₈ H ₆ Cu ₂ I ₂ N ₂
$D_{calc.}/\text{g cm}^{-3}$	3.943	3.998
μ/mm^{-1}	12.060	12.229
Formula Weight	511.03	511.03
Colour	brown	brown
Shape	plate-shaped	plate-shaped
Size/mm ³	0.07×0.03×0.01	0.07×0.03×0.01
T/K	298(2)	298(2)
Crystal System	triclinic	triclinic
Space Group	<i>P</i> -1	<i>P</i> -1
$a/\text{\AA}$	4.2579(2)	4.2434(3)
$b/\text{\AA}$	16.6820(8)	16.6059(13)
$c/\text{\AA}$	12.2725(15)	12.2104(19)
$\alpha/^\circ$	86.288(9)	86.177(15)
$\beta/^\circ$	96.694(9)	96.911(15)
$\gamma/^\circ$	95.230(4)	95.458(7)
$V/\text{\AA}^3$	860.88(12)	848.96(17)
Z	4	4
Z'	2	2
Wavelength/ \AA	0.3185	0.3185
Radiation type	synchrotron	synchrotron
$\theta_{min}/^\circ$	2.166	2.175
$\theta_{max}/^\circ$	11.780	11.774
Measured Refl.	1504	1409
Indep't Refl's	1173	1123
Refl's $I \geq 2\sigma(I)$	794	671
R_{int}	0.0173	0.0229
Parameters	75	75
Restraints	0	0
Largest Peak	1.728	1.702
Deepest Hole	-1.559	-1.788
GooF	1.087	1.061
wR_2 (all data)	0.2177	0.2242
wR_2	0.1939	0.2002
R_1 (all data)	0.0897	0.1038
R_1	0.0657	0.0667

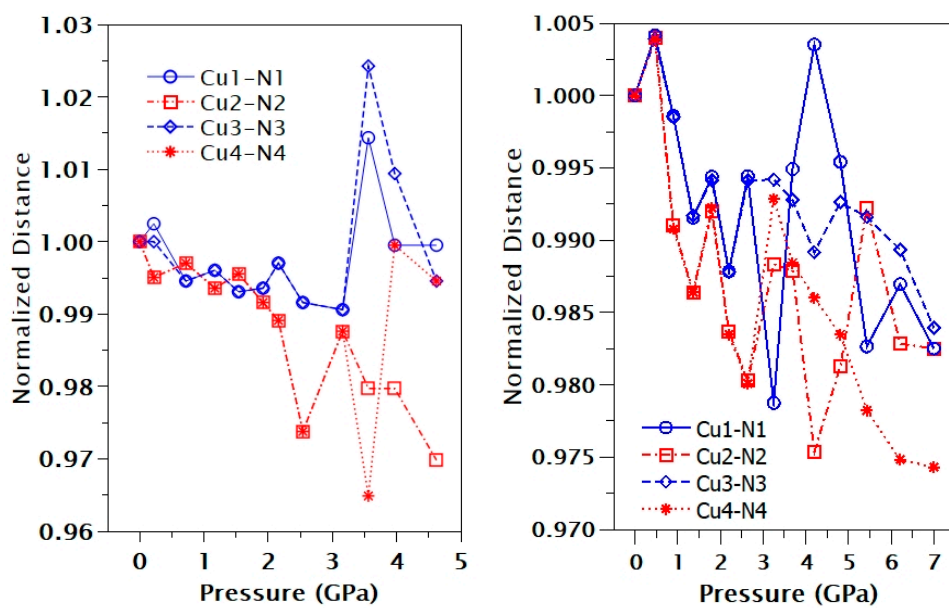


Figure S3. Normalized distances for Cu-N for for $(\text{CuX})_2\text{-Quin}$ ($\text{X}=\text{Br}, \text{I}$) compounds

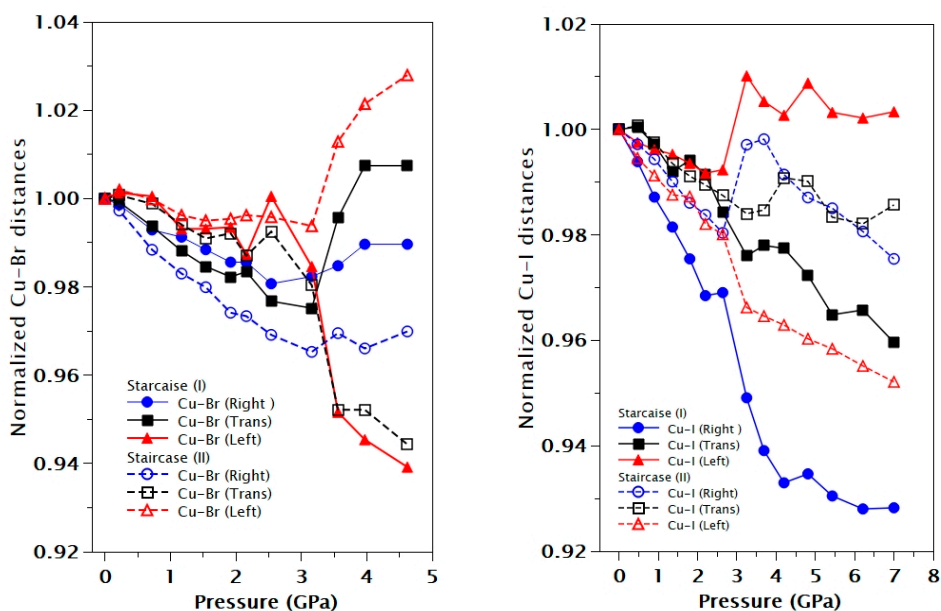


Figure S4. Normalized distances for Cu-X for for $(\text{CuX})_2\text{-Quin}$ ($\text{X}=\text{Br}, \text{I}$) compounds

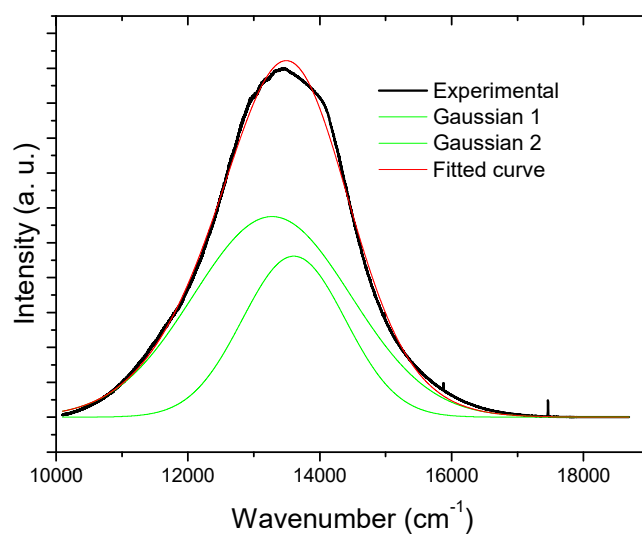
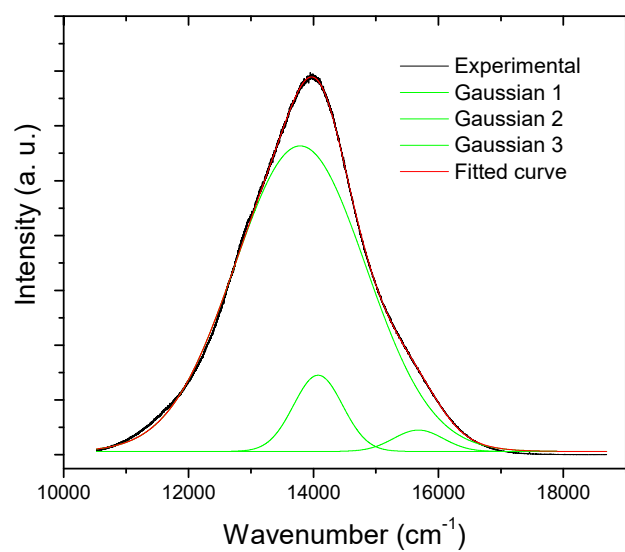


Figure S5. Room temperature emission spectrum fitted to three Gaussians for (CuBr)₂-Quin (top) and (CuIr)₂-Quin (bottom) compounds