Polymeric copper(I)–NHC complexes with bulky bidentate (N^C) ligands: synthesis and solid-state luminescence

ELECTRONIC SUPPLEMENTARY INFORMATION

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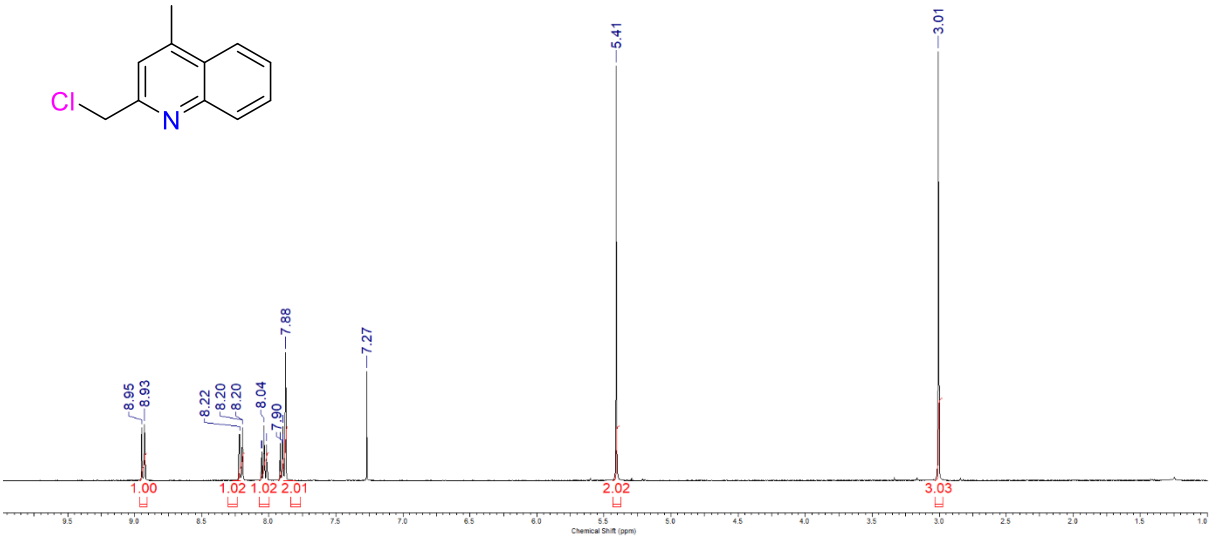
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1.02
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2.01
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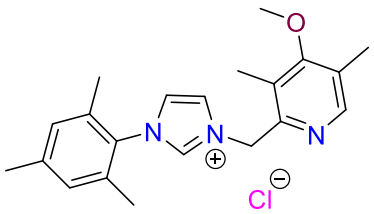
3.03
Chemical Shift (ppm)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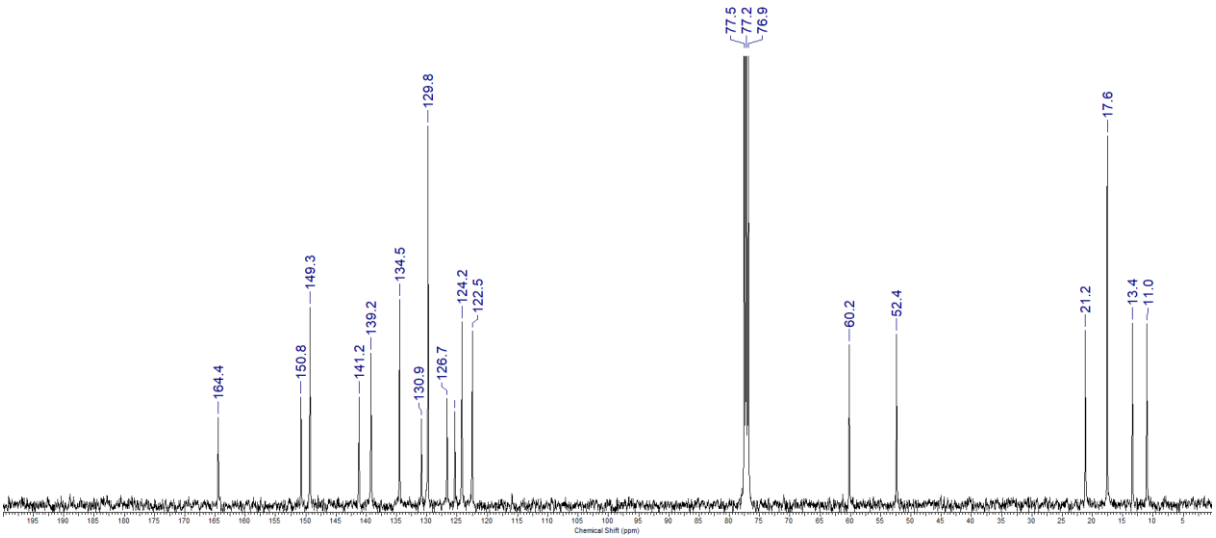
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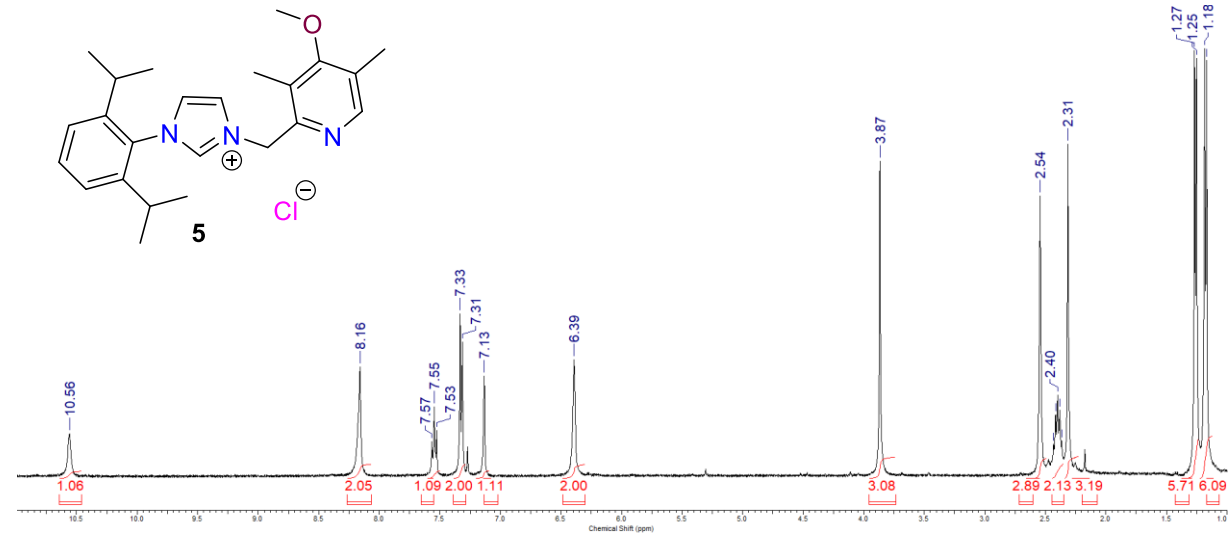
Chemical Shift (ppm)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1.25
1.18
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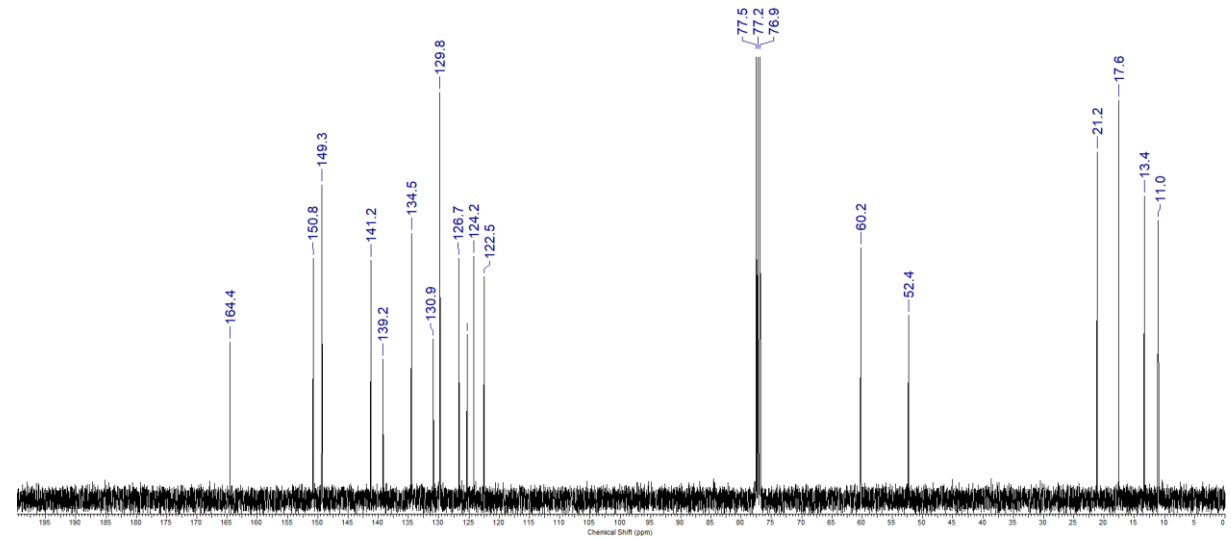
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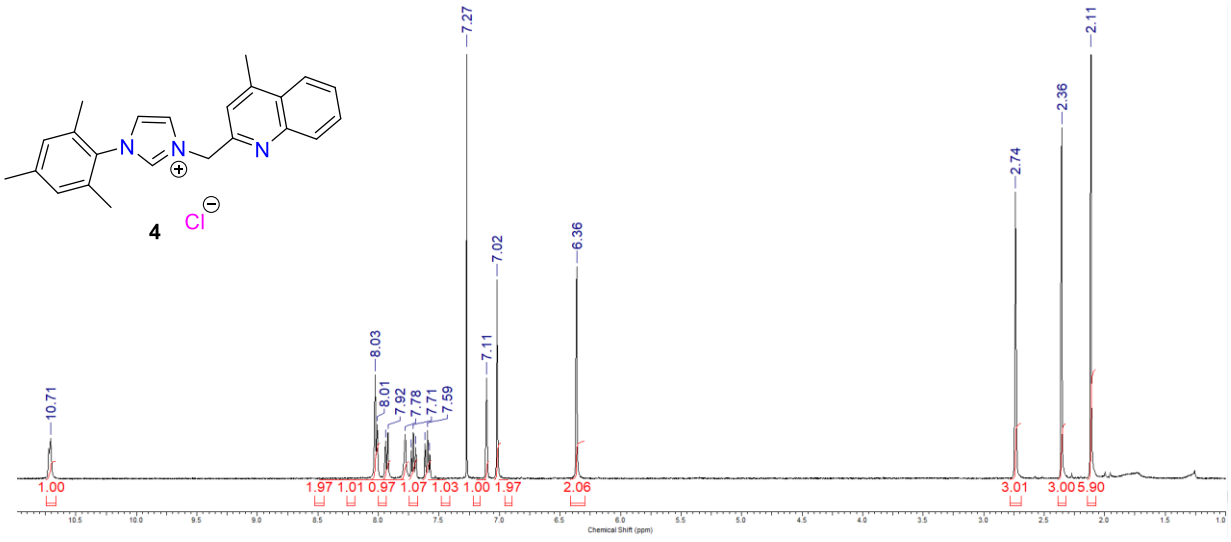
Chemical Shift (ppm)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2.36
2.11
1.00
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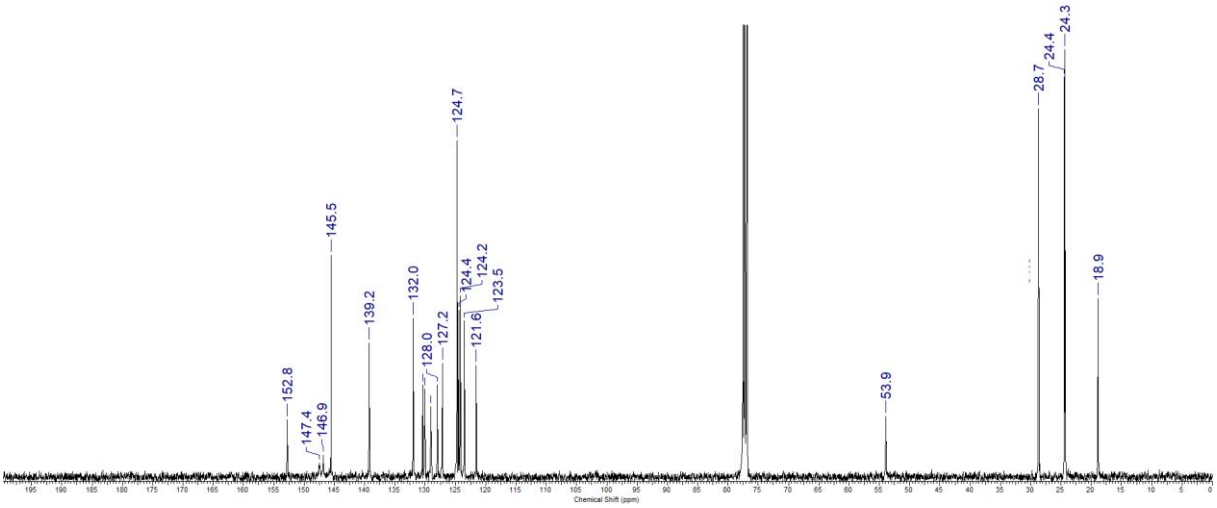
Chemical Shift (ppm)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24.3
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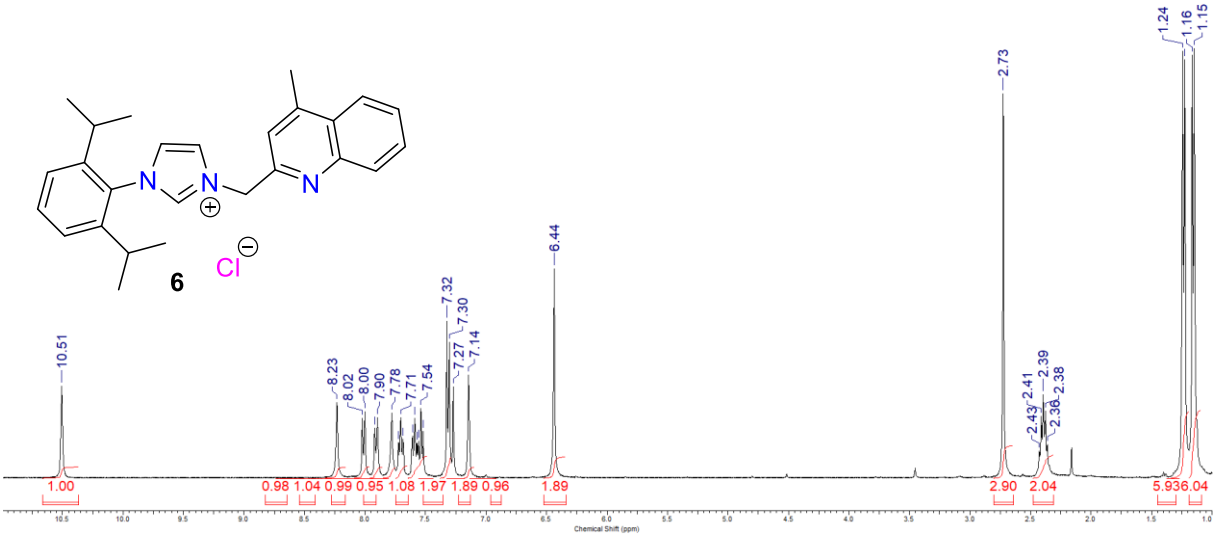
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Cl
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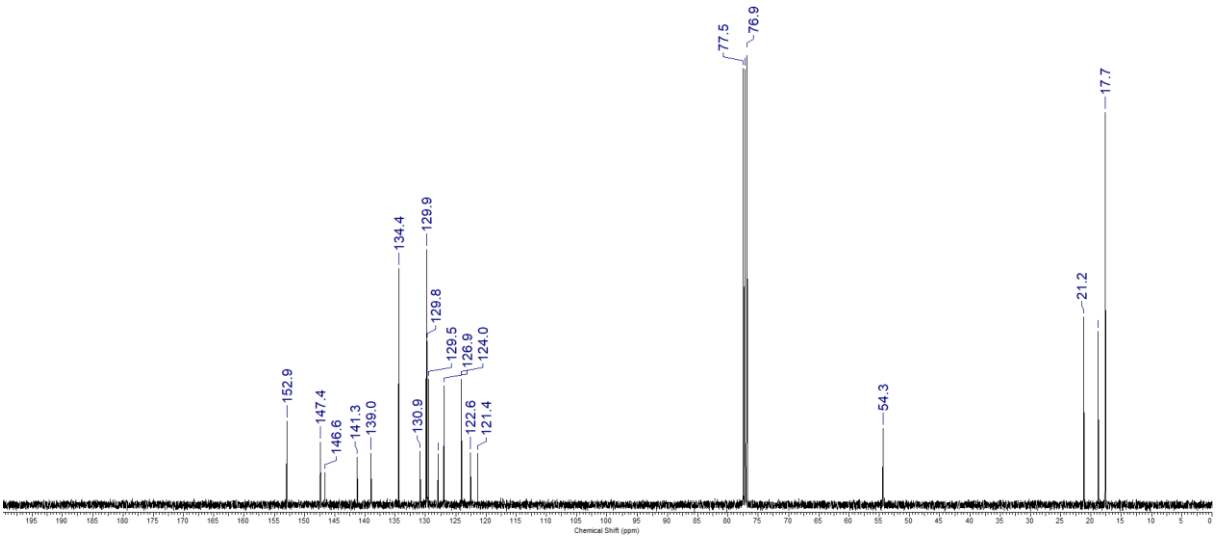
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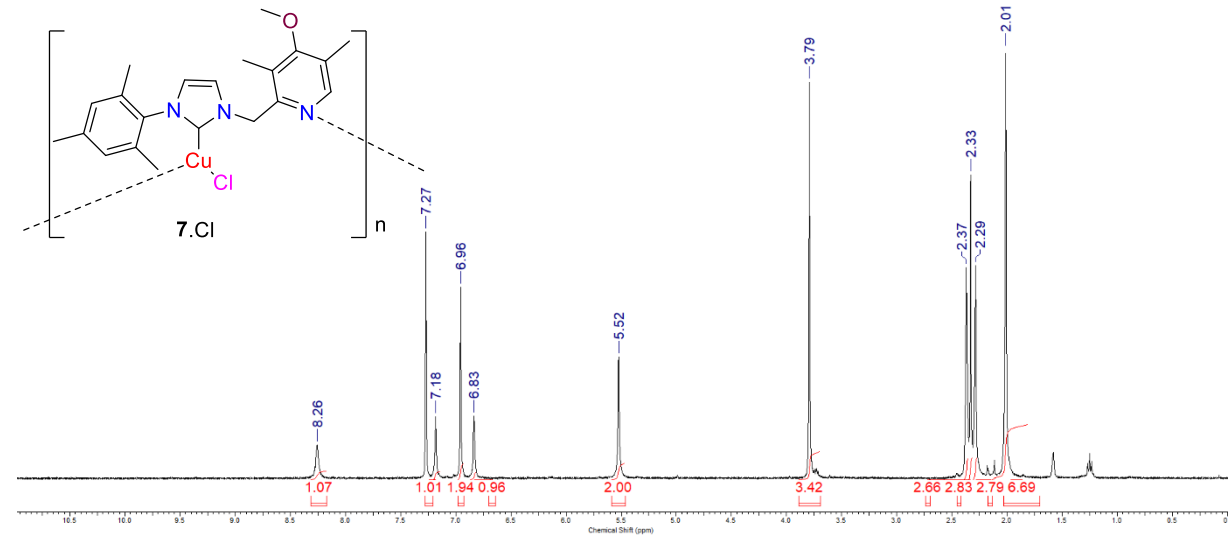
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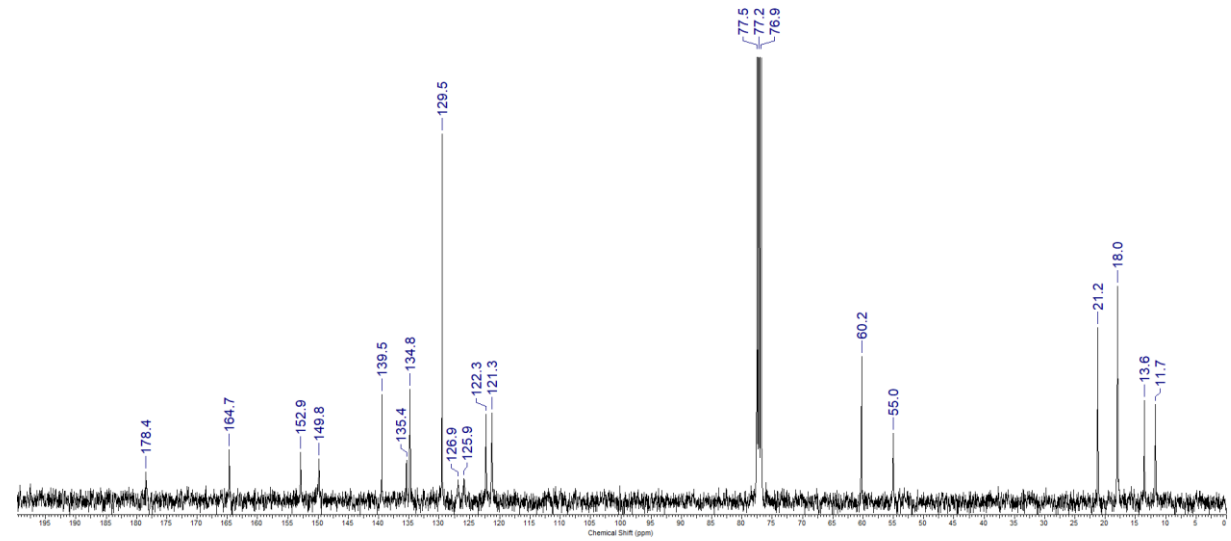
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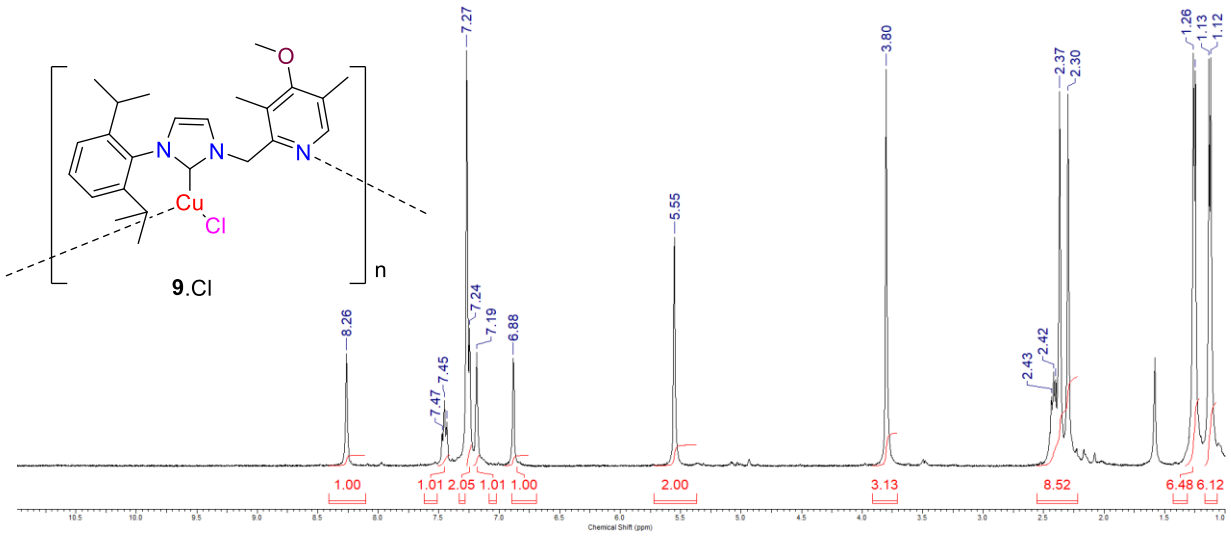
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2.42
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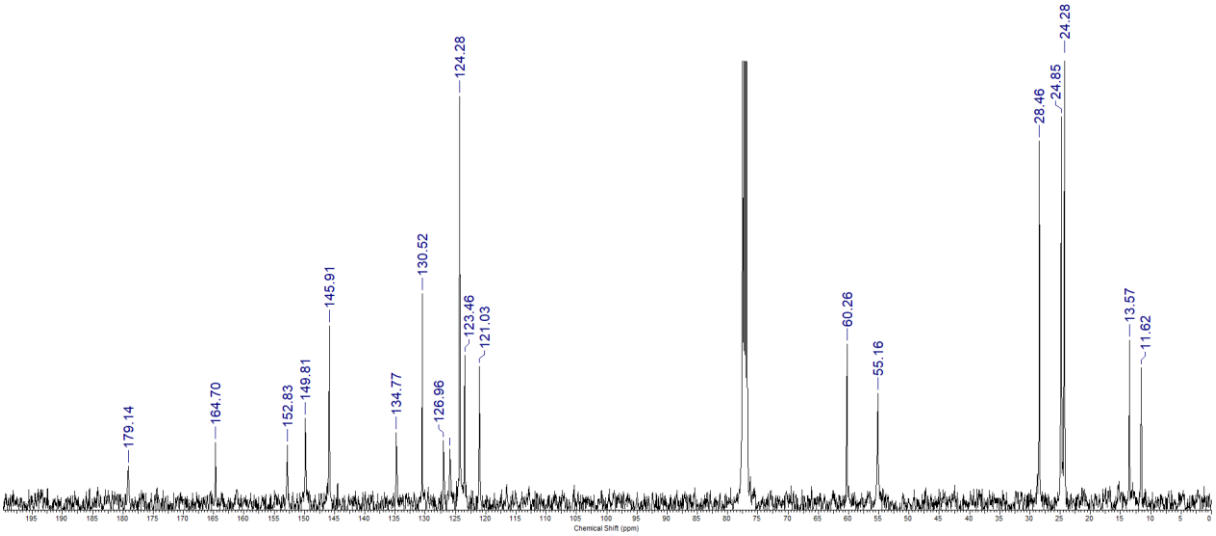
6.12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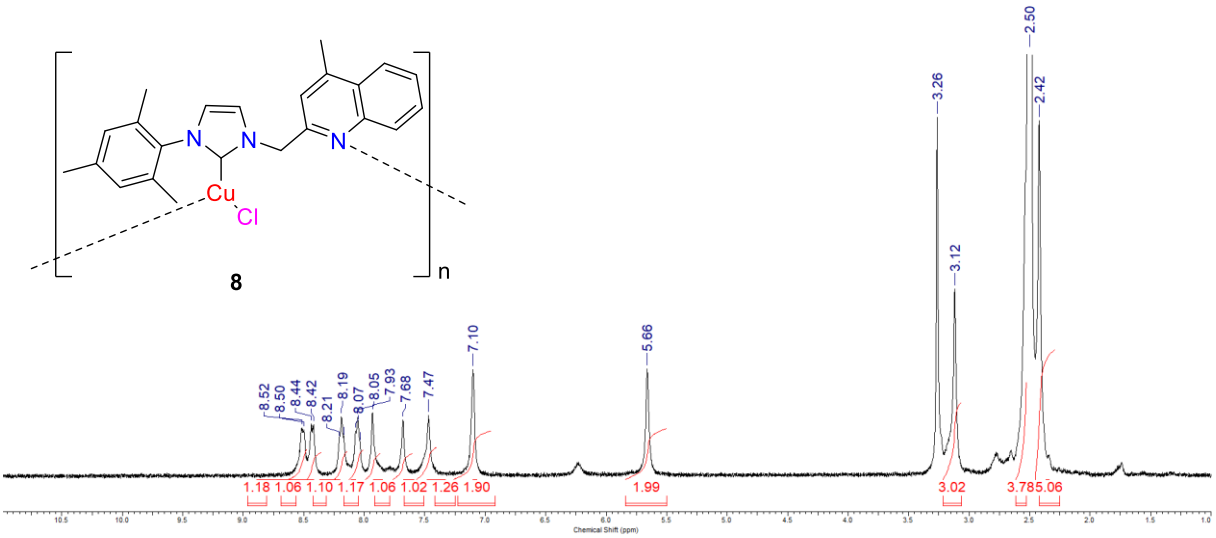
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N
Cu
Cl
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8
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7.68
7.47
7.10
5.66
3.26
3.12
2.50
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3.02
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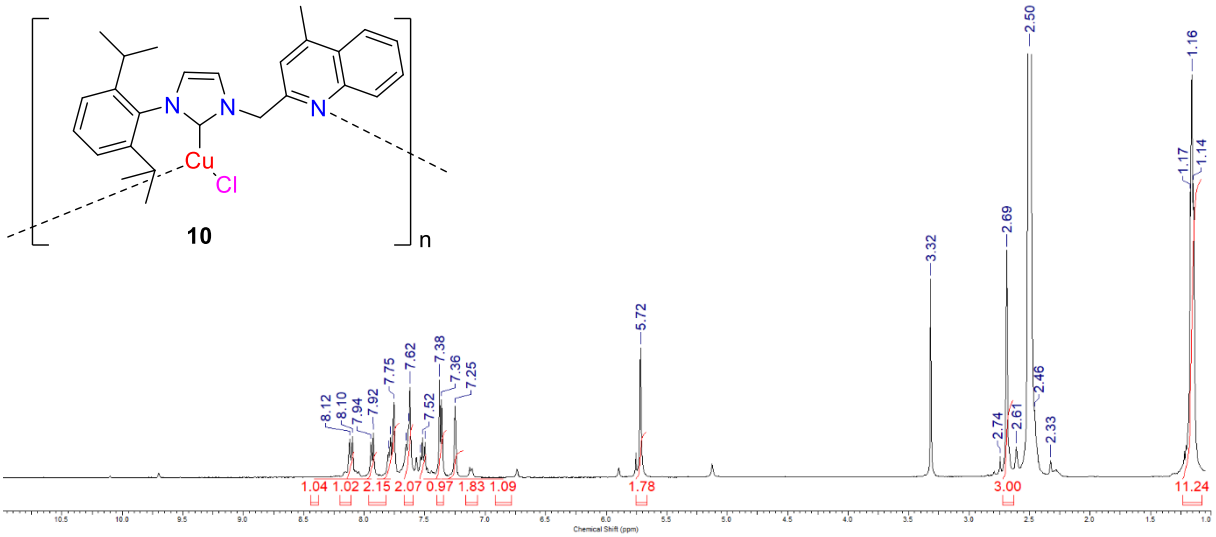
Chemical Shift (ppm)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7.25
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3.32
2.69
2.74
2.61
2.50
2.46
2.33
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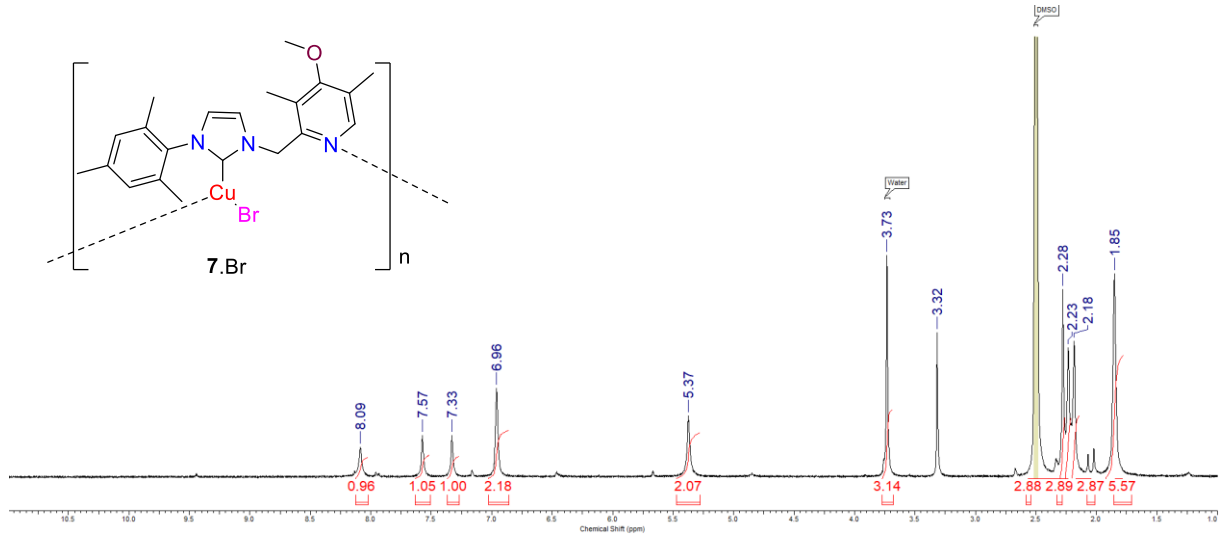
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N
Cu
Br
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7.33
6.96
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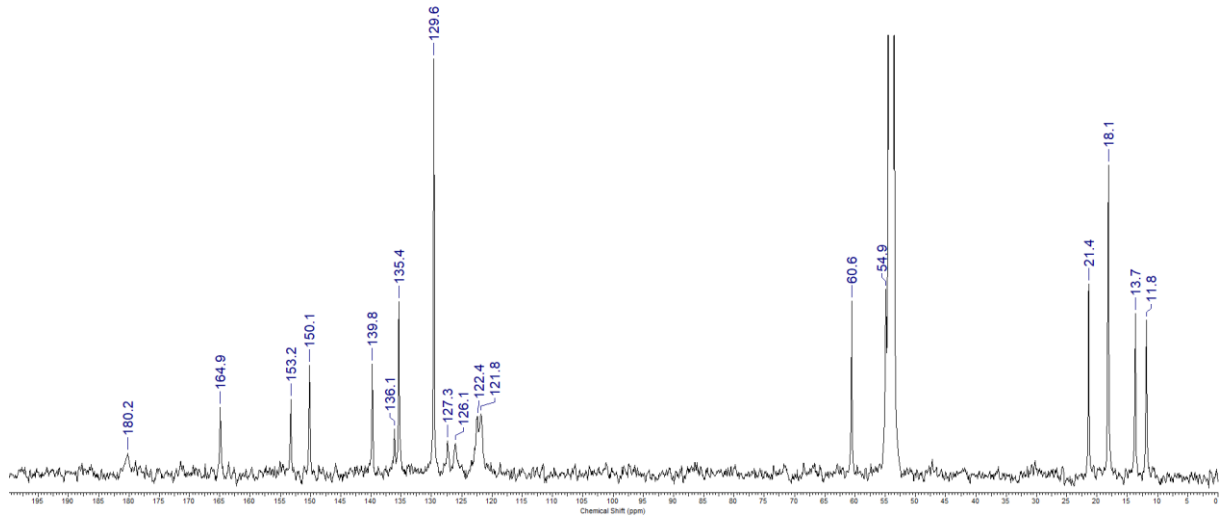
Chemical Shift (ppm)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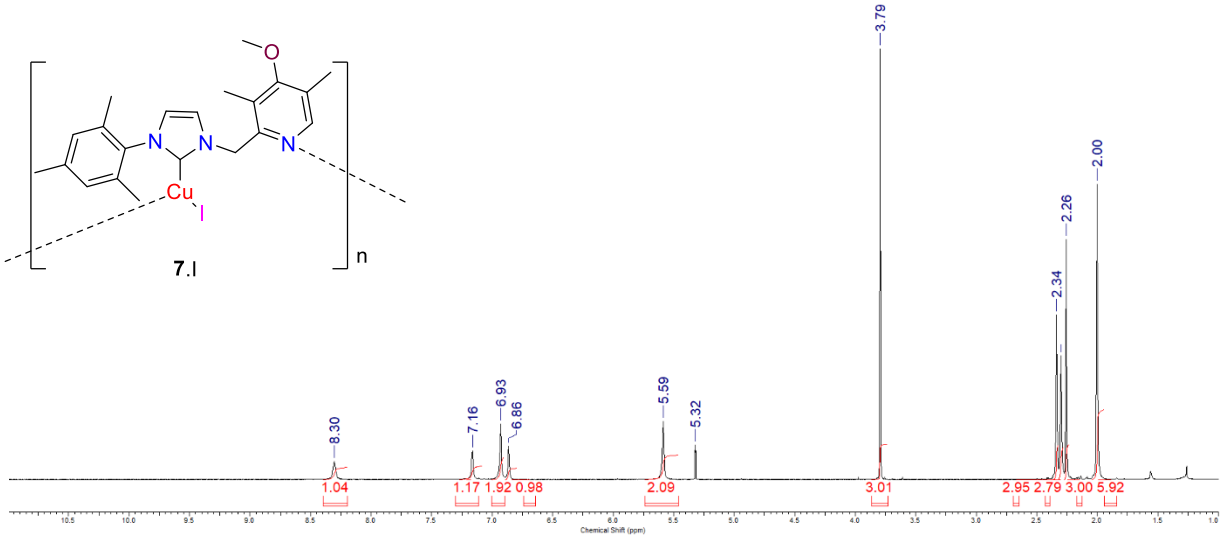
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N
Cu
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5.59
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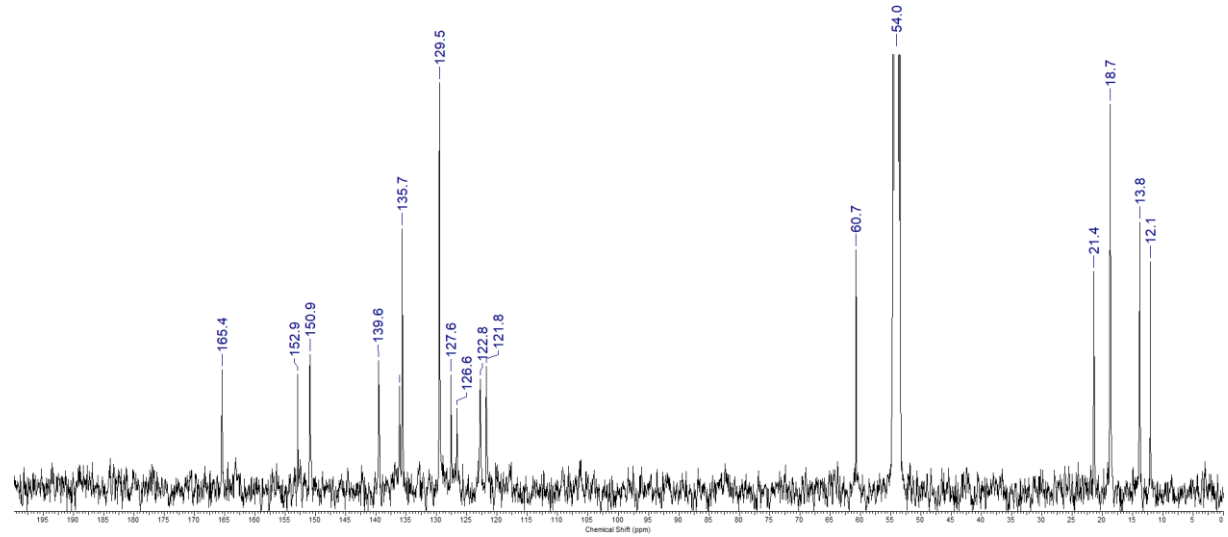
3.00
5.92
Chemical Shift (ppm)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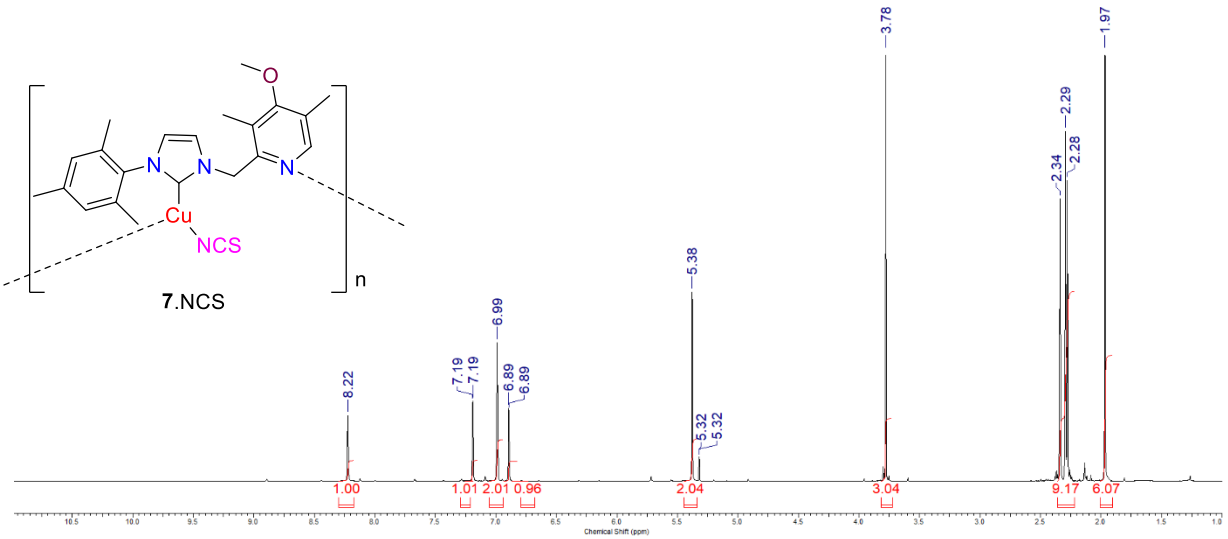
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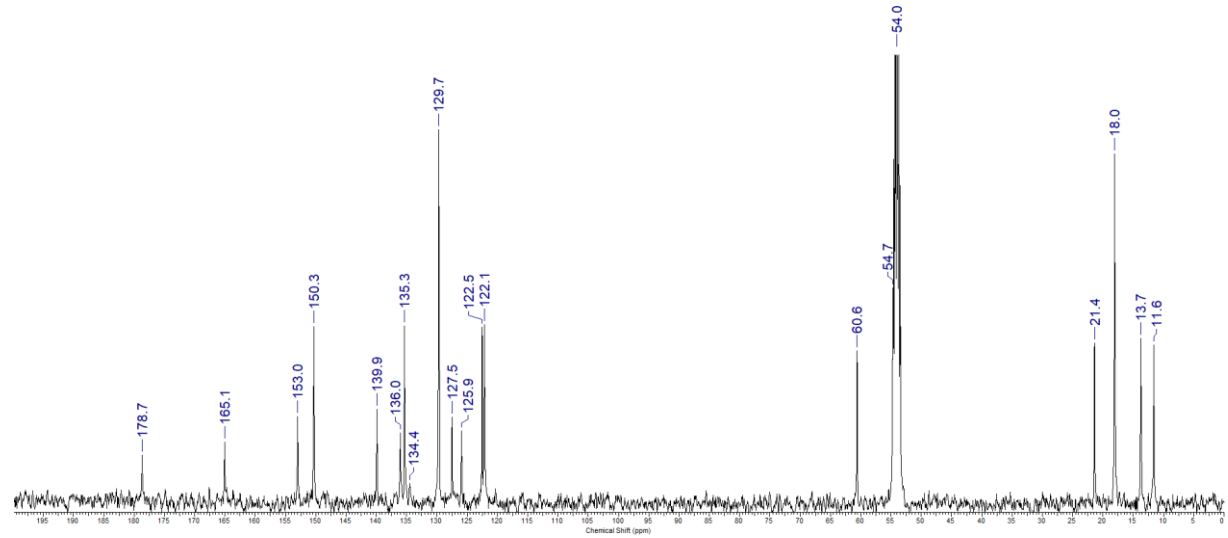
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11.6
Chemical Shift (ppm)

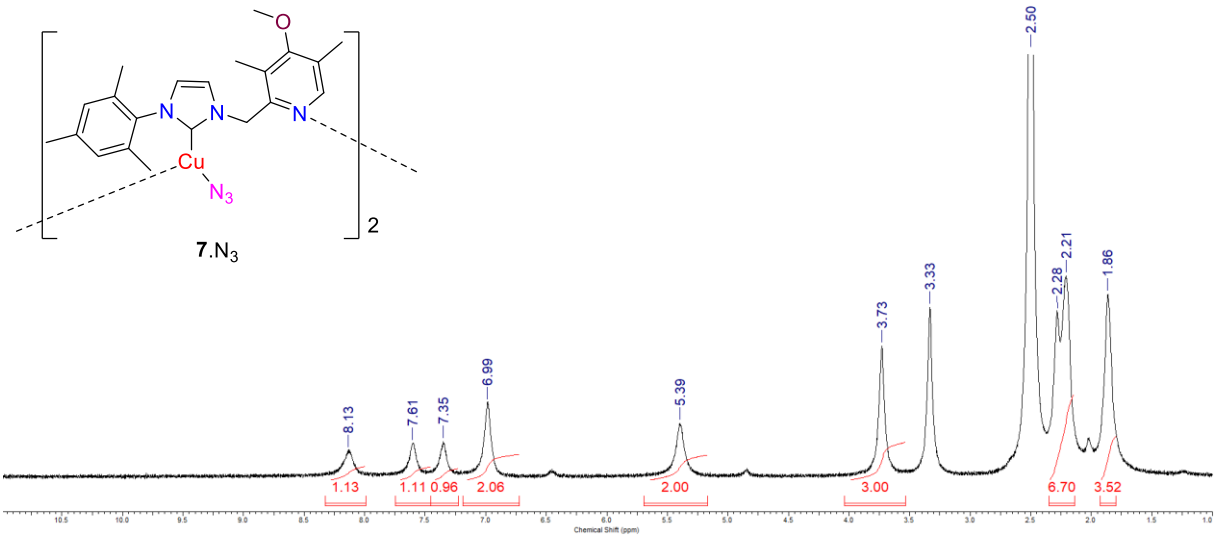


Fig. S1 ^{1}H- and ^{13}C-NMR spectra of all compounds

Table S1. Sample and crystal refinement data for 7.Cl

Chemical formula	$C_{21}H_{25}ClCuN_3O$
Formula weight	434.43 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.110 x 0.239 x 0.504 mm
Crystal system	monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	a = 14.3299(15) Å α = 90°
	b = 9.6126(10) Å β = 90.387(4)°
	c = 14.9035(16) Å γ = 90°
Volume	2052.9(4) $Å^3$
Z	4
Density (calculated)	1.406 g/cm^3
Absorption coefficient	1.209 mm^{-1}
F(000)	904
Theta range for data collection	1.97 to 30.51°
Index ranges	-20<=h<=20, -13<=k<=13, -21<=l<=21
Reflections collected	168008
Independent reflections	6281 [R(int) = 0.0900]
Coverage of independent reflections	100.0%
Absorption correction	Numerical
Max. and min. transmission	0.8780 and 0.5810
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6281 / 0 / 250
Goodness-of-fit on F^2	1.030
Δ/σ_{max}	0.001
Final R indices	5179 data; I>2σ(I) R1 = 0.0311, wR2 = 0.0722
	all data R1 = 0.0449, wR2 = 0.0795
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0286P)^2+2.2658P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.508 and -0.469 $eÅ^{-3}$
R.M.S. deviation from mean	0.075 $eÅ^{-3}$

Table S2. Sample and crystal refinement data for 8

Chemical formula	$C_{24}H_{25}Cl_3CuN_3$
Formula weight	525.36 g/mol
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal size	0.196 x 0.245 x 0.390 mm
Crystal system	monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	a = 13.8969(14) Å α = 90°
	b = 10.5381(11) Å β = 108.907(3)°
	c = 17.6009(17) Å γ = 90°
Volume	2438.5(4) $Å^3$
Z	4
Density (calculated)	1.431 g/cm^3
Absorption coefficient	1.241 mm^{-1}
F(000)	1080
Theta range for data collection	2.26 to 32.83°
Index ranges	-21<=h<=21, -15<=k<=15, -26<=l<=26
Reflections collected	99517
Independent reflections	8772 [R(int) = 0.0524]
Coverage of independent reflections	96.7%
Absorption correction	Numerical
Max. and min. transmission	0.7930 and 0.6430
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	8772 / 0 / 380
Goodness-of-fit on F^2	1.027
Δ/σ_{max}	0.001
Final R indices	7009 data; I>2σ(I) R1 = 0.0324, wR2 = 0.0799
	all data R1 = 0.0465, wR2 = 0.0867
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0402P)^2+1.0651P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.711 and -0.699 $eÅ^{-3}$
R.M.S. deviation from mean	0.068 $eÅ^{-3}$

Table S3. Sample and crystal refinement data for 9

Chemical formula	$C_{24}H_{31}ClCuN_3O$	
Formula weight	476.51 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.230 x 0.262 x 0.266 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 10.5133(13) Å	α = 90°
	b = 12.5355(15) Å	β = 98.654(4)°
	c = 17.866(2) Å	γ = 90°
Volume	2327.7(5) $Å^3$	
Z	4	
Density (calculated)	1.360 g/cm^3	
Absorption coefficient	1.073 mm^{-1}	
F(000)	1000	
Theta range for data collection	2.42 to 27.48°	
Index ranges	-13<=h<=13, -16<=k<=16, -23<=l<=23	
Reflections collected	82654	
Independent reflections	5337 [R(int) = 0.0387]	
Coverage of independent reflections	99.9%	
Absorption correction	Numerical	
Max. and min. transmission	0.7900 and 0.7630	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5337 / 0 / 278	
Goodness-of-fit on F^2	1.057	
Δ/σ_{max}	0.001	
Final R indices	4757 data; I>2σ(I)	R1 = 0.0354, wR2 = 0.0899
	all data	R1 = 0.0409, wR2 = 0.0935
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0432P)^2+2.8561P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.648 and -0.754 $eÅ^{-3}$	
R.M.S. deviation from mean	0.079 $eÅ^{-3}$	

Table S4. Sample and crystal refinement data for 10

Chemical formula	$C_{26}H_{29}ClCuN_3$
Formula weight	482.51 g/mol
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal size	0.098 x 0.142 x 0.198 mm
Crystal system	monoclinic
Space group	P 21/c
Unit cell dimensions	a = 13.1798(15) Å α = 90°
	b = 14.1584(16) Å β = 97.399(11)°
	c = 12.8105(15) Å γ = 90°
Volume	2370.6(5) $Å^3$
Z	4
Density (calculated)	1.352 g/cm^3
Absorption coefficient	1.052 mm^{-1}
F(000)	1008
Theta range for data collection	2.54 to 33.14°
Index ranges	-19<=h<=19, -21<=k<=20, -19<=l<=18
Reflections collected	196946
Independent reflections	8400 [R(int) = 0.3990]
Coverage of independent reflections	93.1%
Absorption correction	Numerical
Max. and min. transmission	0.9040 and 0.8190
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	8400 / 0 / 285
Goodness-of-fit on F^2	0.933
Δ/σ_{max}	0.001
Final R indices	2889 data; I>2σ(I) R1 = 0.0742, wR2 = 0.1536
	all data R1 = 0.2849, wR2 = 0.2342
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1050P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.00(4)
Largest diff. peak and hole	0.427 and -0.612 $eÅ^{-3}$
R.M.S. deviation from mean	0.098 $eÅ^{-3}$

Table S5. Sample and crystal refinement data for 7.Br

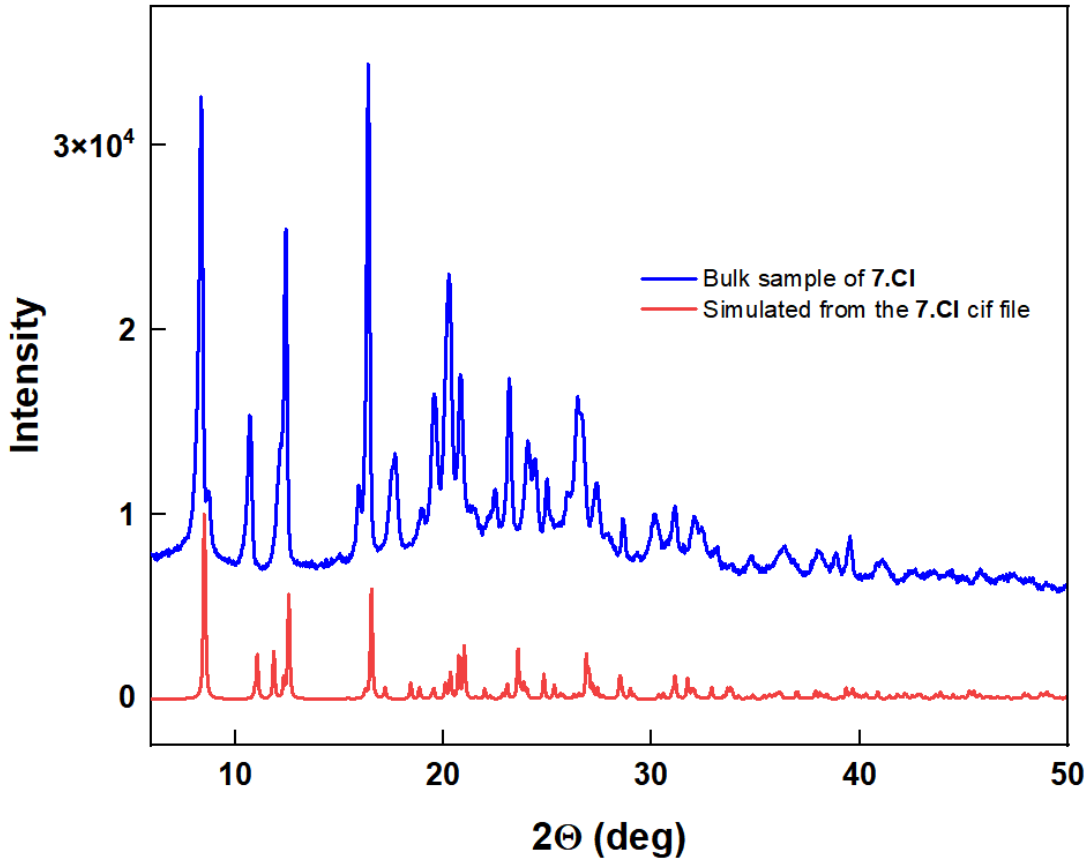
Chemical formula	$C_{21}H_{25}BrCuN_3O$
Formula weight	478.89 g/mol
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal size	0.149 x 0.153 x 0.196 mm
Crystal system	monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	a = 14.5159(16) Å α = 90° b = 9.8890(11) Å β = 91.637(4)° c = 14.8049(16) Å γ = 90°
Volume	2124.3(4) $Å^3$
Z	4
Density (calculated)	1.497 g/cm^3
Absorption coefficient	2.924 mm^{-1}
F(000)	976
Theta range for data collection	2.75 to 30.59°
Index ranges	-20<=h<=20, -14<=k<=14, -21<=l<=20
Reflections collected	81002
Independent reflections	6476 [R(int) = 0.0450]
Coverage of independent reflections	99.0%
Absorption correction	Numerical
Max. and min. transmission	0.6700 and 0.5980
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6476 / 0 / 250
Goodness-of-fit on F^2	1.031
Δ/σ_{max}	0.001
Final R indices	5126 data; I>2σ(I) R1 = 0.0313, wR2 = 0.0729 all data R1 = 0.0473, wR2 = 0.0798
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0370P)^2+1.3533P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.070 and -0.535 $eÅ^{-3}$
R.M.S. deviation from mean	0.079 $eÅ^{-3}$

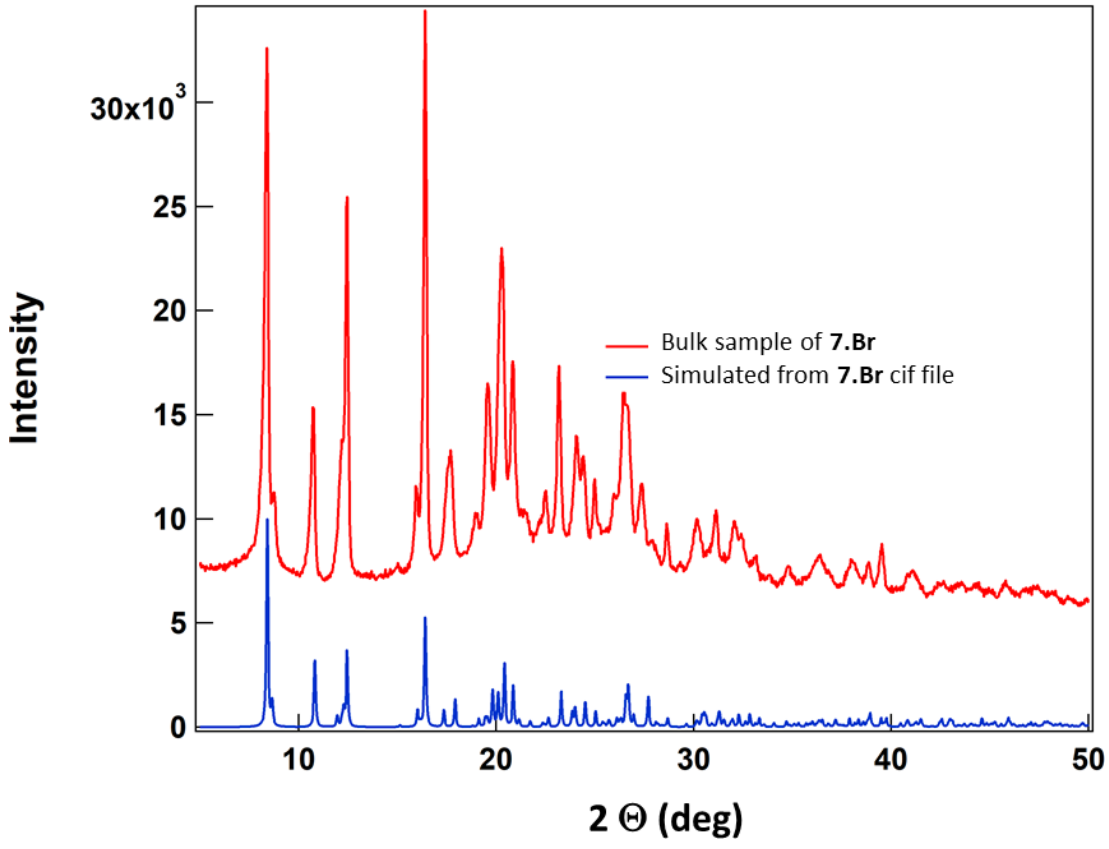
Table S6. Sample and crystal data for 7.N_3

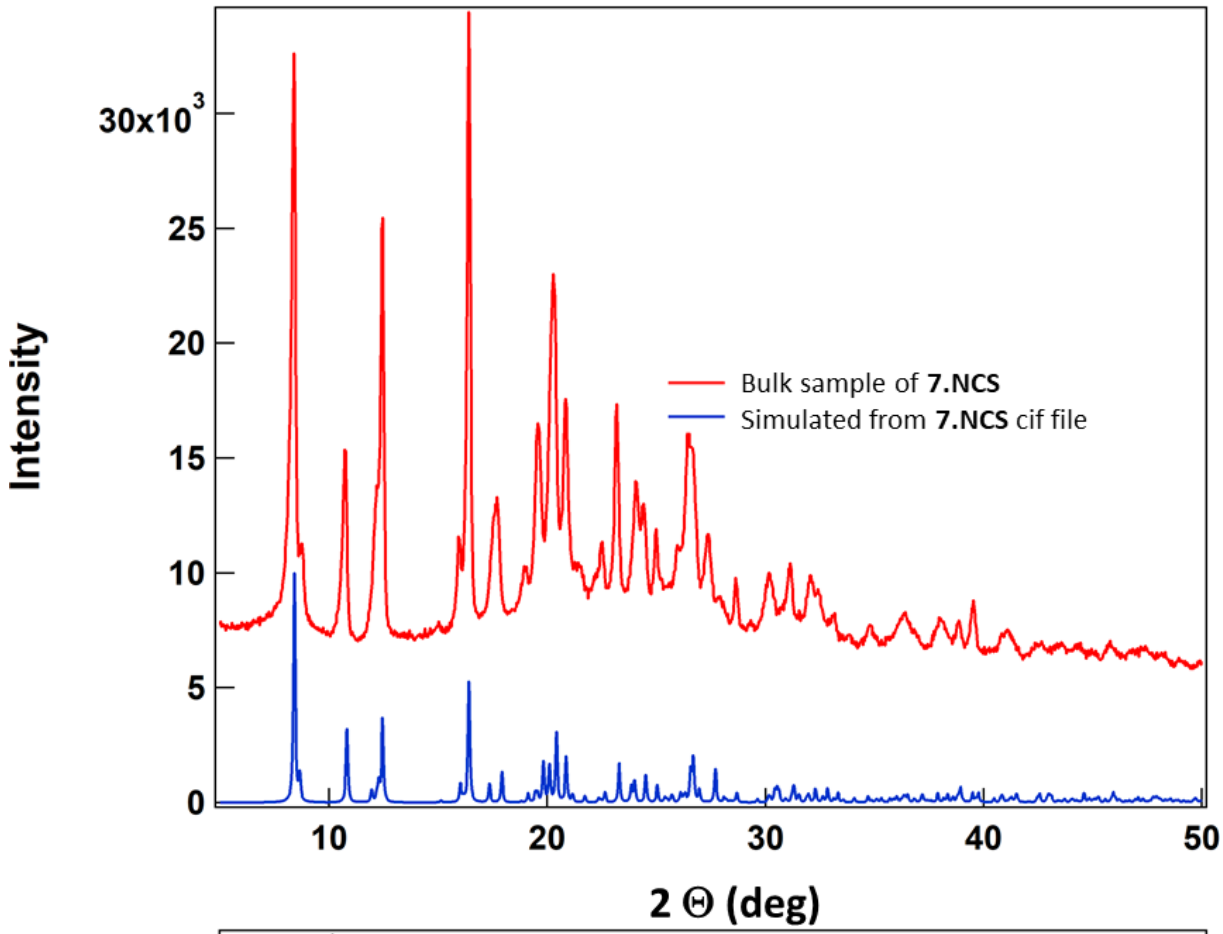
Chemical formula	$C_{44}H_{54}Cl_4Cu_2N_{12}O_2$
Formula weight	1051.87 g/mol
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal size	0.122 x 0.131 x 0.228 mm
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 10.2745(7) Å α = 91.902(4)°
	b = 11.2131(7) Å β = 93.379(4)°
	c = 11.3294(8) Å γ = 113.401(3)°
Volume	1193.52(14) $Å^3$
Z	1
Density (calculated)	1.463 g/cm^3
Absorption coefficient	1.166 mm^{-1}
F(000)	544
Theta range for data collection	2.60 to 30.62°
Index ranges	-14<=h<=14, -15<=k<=16, -16<=l<=16
Reflections collected	92223
Independent reflections	7307 [R(int) = 0.0675]
Coverage of independent reflections	98.9%
Absorption correction	Numerical
Max. and min. transmission	0.8710 and 0.7770
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7307 / 0 / 315
Goodness-of-fit on F^2	1.021
Final R indices	4788 data; I>2σ(I) R1 = 0.0616, wR2 = 0.1604
	all data R1 = 0.1037, wR2 = 0.1885
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0913P)^2+1.6021P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	2.054 and -1.243 $eÅ^{-3}$
R.M.S. deviation from mean	0.094 $eÅ^{-3}$

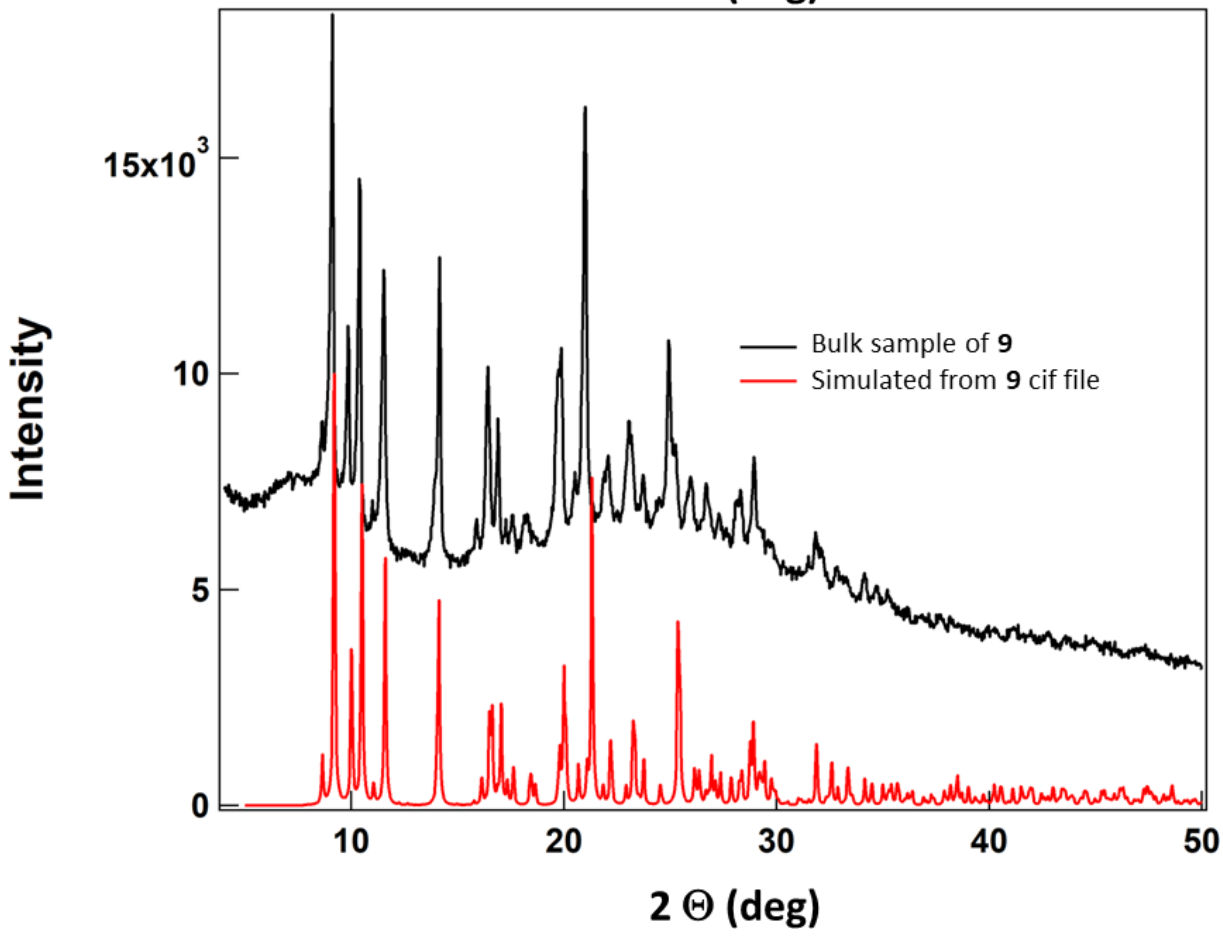
Table S7. Sample and crystal refinement data for 7.NCS

Chemical formula	$C_{22}H_{25}CuN_4OS$	
Formula weight	457.06 g/mol	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.217 x 0.999 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 11.7265(16) Å	α = 90°
	b = 10.3870(14) Å	β = 105.032(4)°
	c = 18.401(2) Å	γ = 90°
Volume	2164.6(5) $Å^3$	
Z	4	
Density (calculated)	1.402 g/cm^3	
Absorption coefficient	1.126 mm^{-1}	
F(000)	952	
Theta range for data collection	2.29 to 27.48°	
Index ranges	-15<=h<=15, -13<=k<=13, -23<=l<=23	
Reflections collected	74975	
Independent reflections	4966 [R(int) = 0.0447]	
Coverage of independent reflections	99.9%	
Absorption correction	Numerical	
Max. and min. transmission	0.8960 and 0.3990	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4966 / 0 / 335	
Goodness-of-fit on F^2	1.048	
Δ/σ_{max}	0.002	
Final R indices	4169 data; I>2σ(I)	R1 = 0.0298, wR2 = 0.0775
	all data	R1 = 0.0397, wR2 = 0.0831
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0401P)^2+1.2771P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.297 and -0.298 $eÅ^{-3}$	
R.M.S. deviation from mean	0.055 $eÅ^{-3}$	


3×10^4
2
1
0
Intensity
Bulk sample of 7.Cl
Simulated from the 7.Cl cif file
10
20
30
40
50
2Θ (deg)


30x10^3
25
20
15
10
5
0
Intensity
Bulk sample of 7.Br
Simulated from 7.Br cif file
10
20
30
40
50
2 Θ (deg)


30x10^3
25
20
15
10
5
0
Intensity
Bulk sample of 7.NCS
Simulated from 7.NCS cif file
10
20
30
40
50
2 Θ (deg)


15x10^3
10
5
0
Intensity
Bulk sample of 9
Simulated from 9 cif file
10
20
30
40
50
2 Θ (deg)

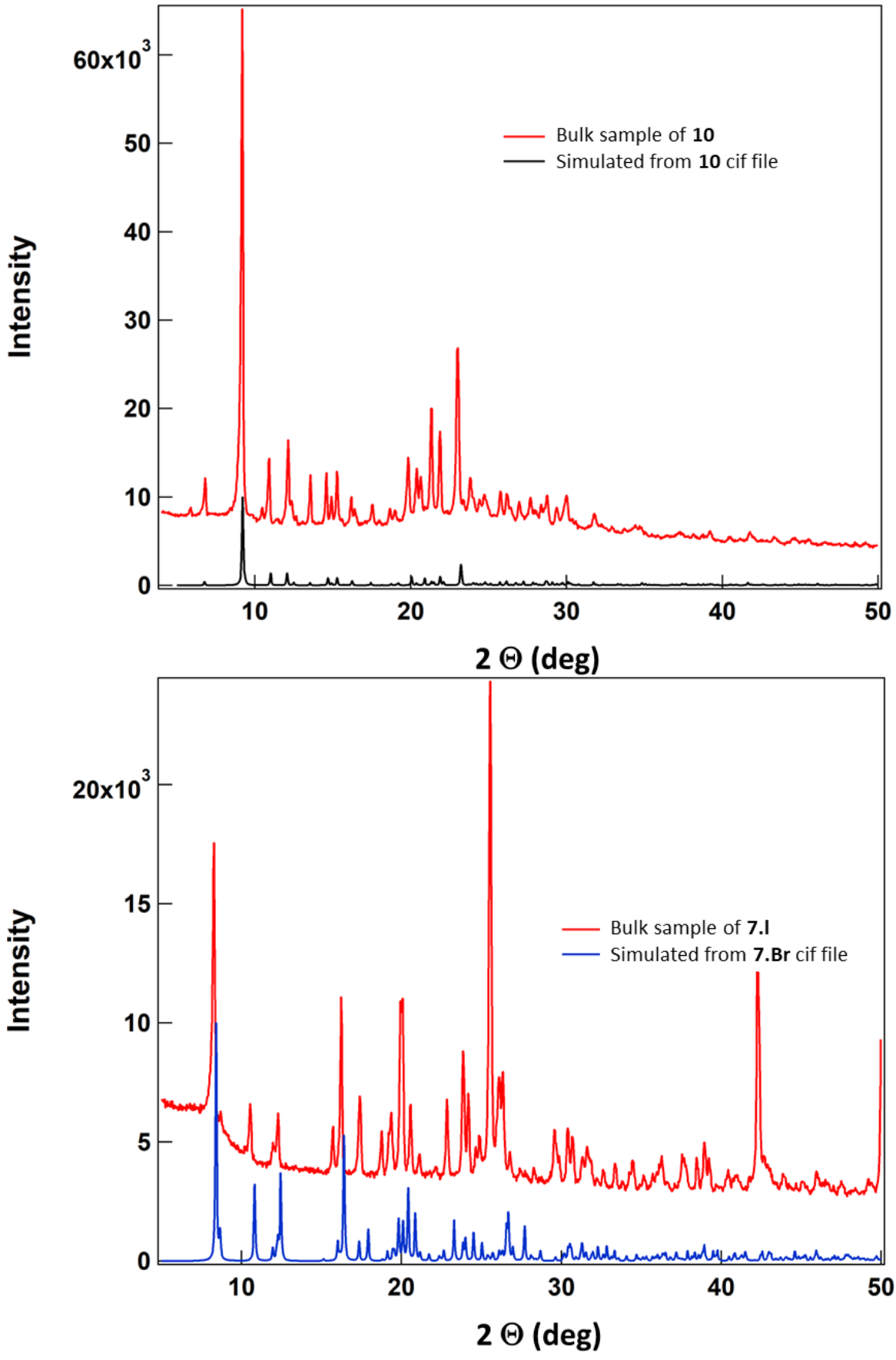


Figure S2: Simulated and experimental PXRD data

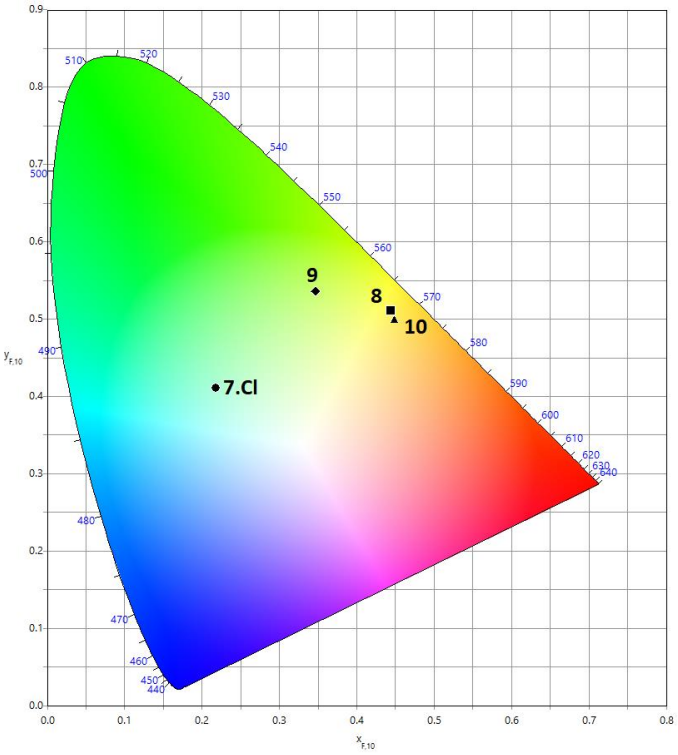


Fig. S3 CIE diagram for the variation N^C ligand (halide = Cl^-).

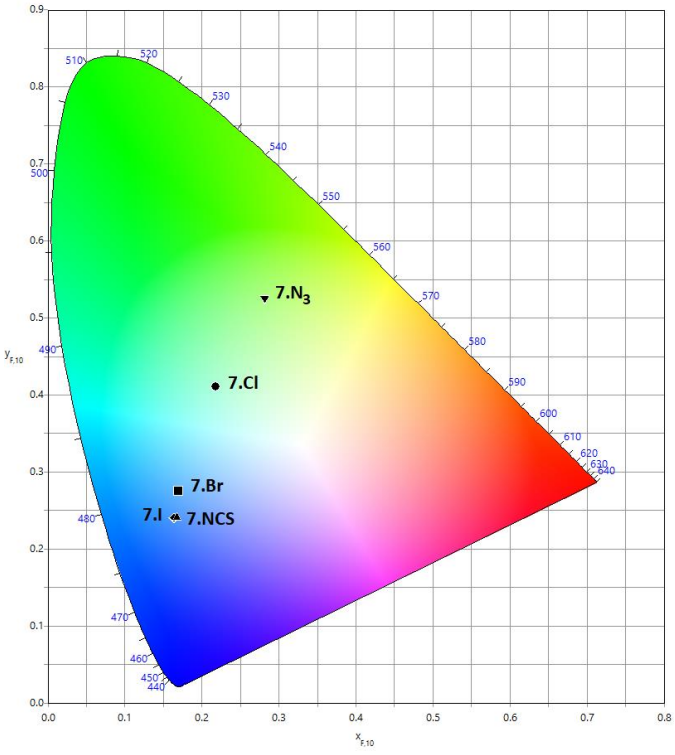
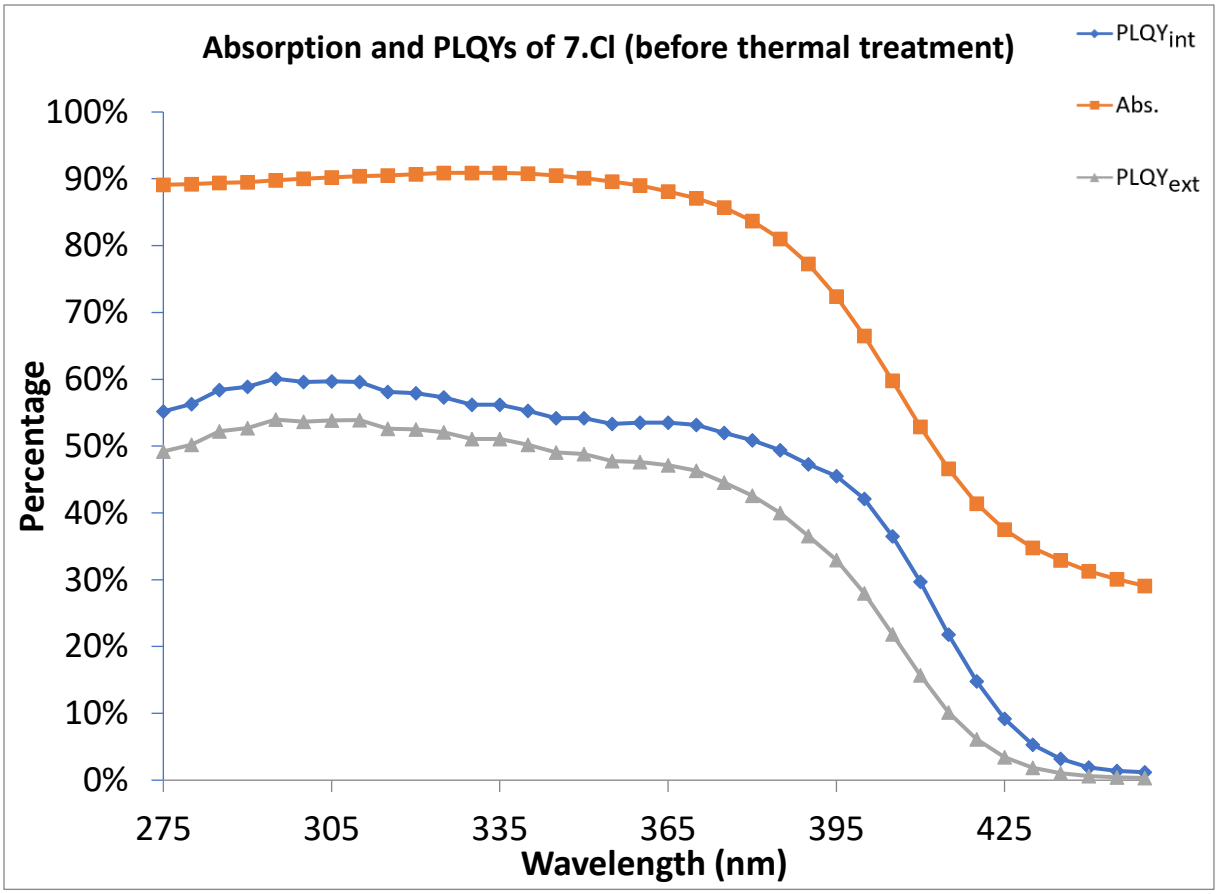
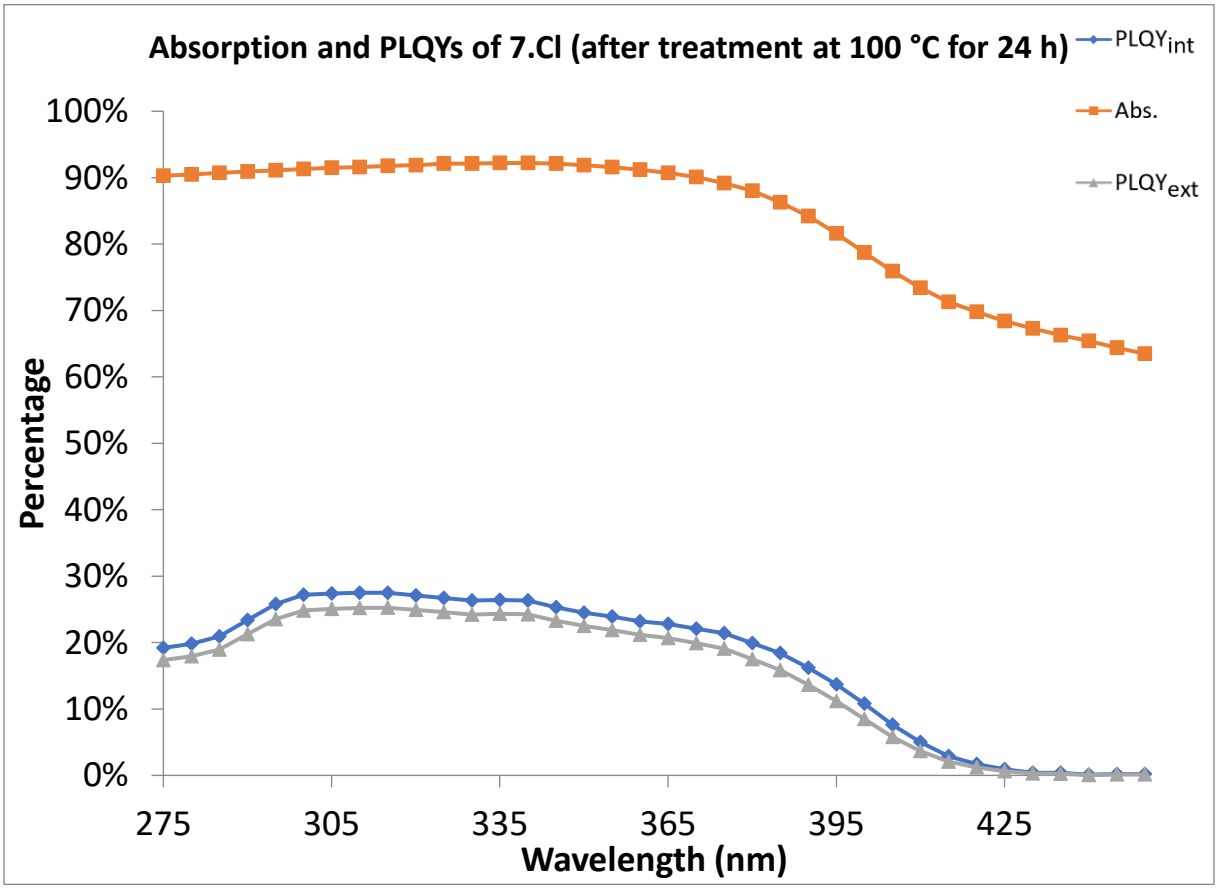
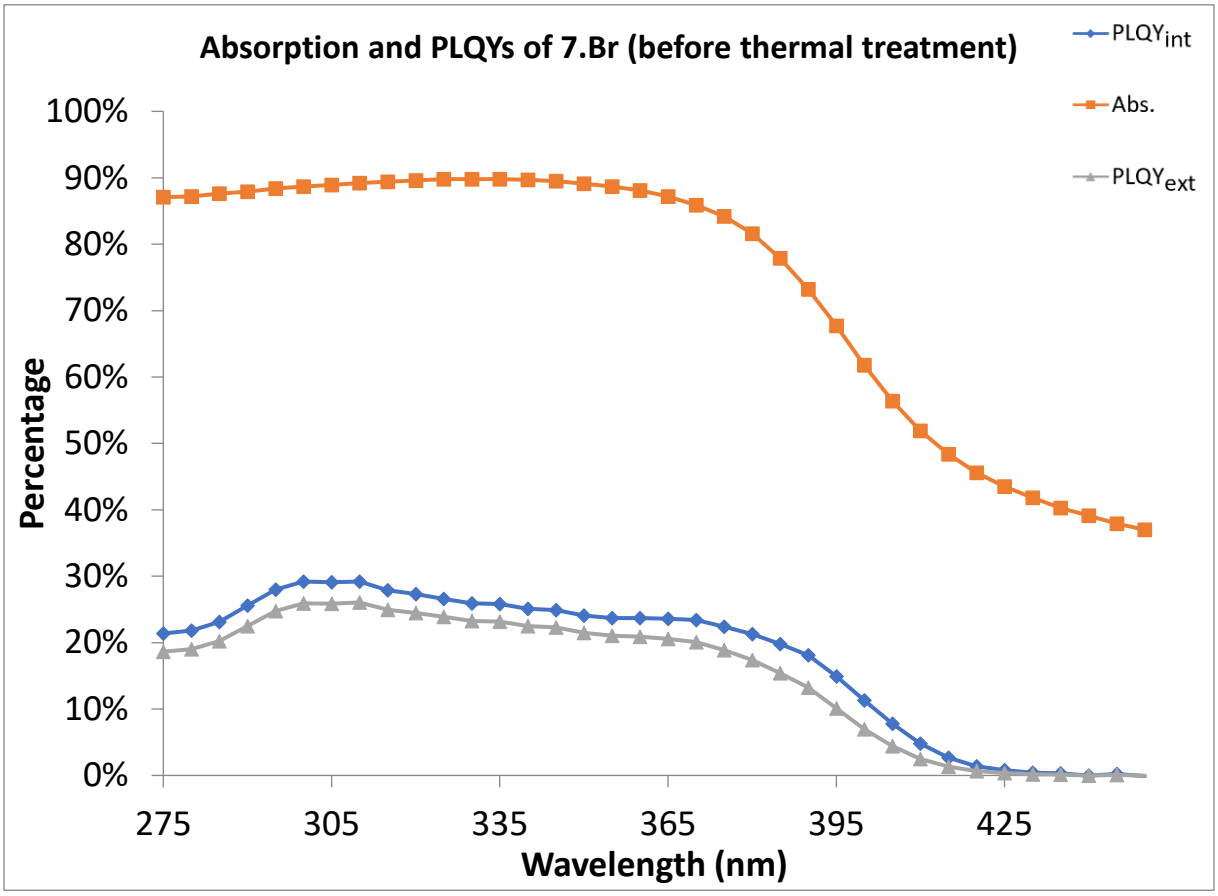
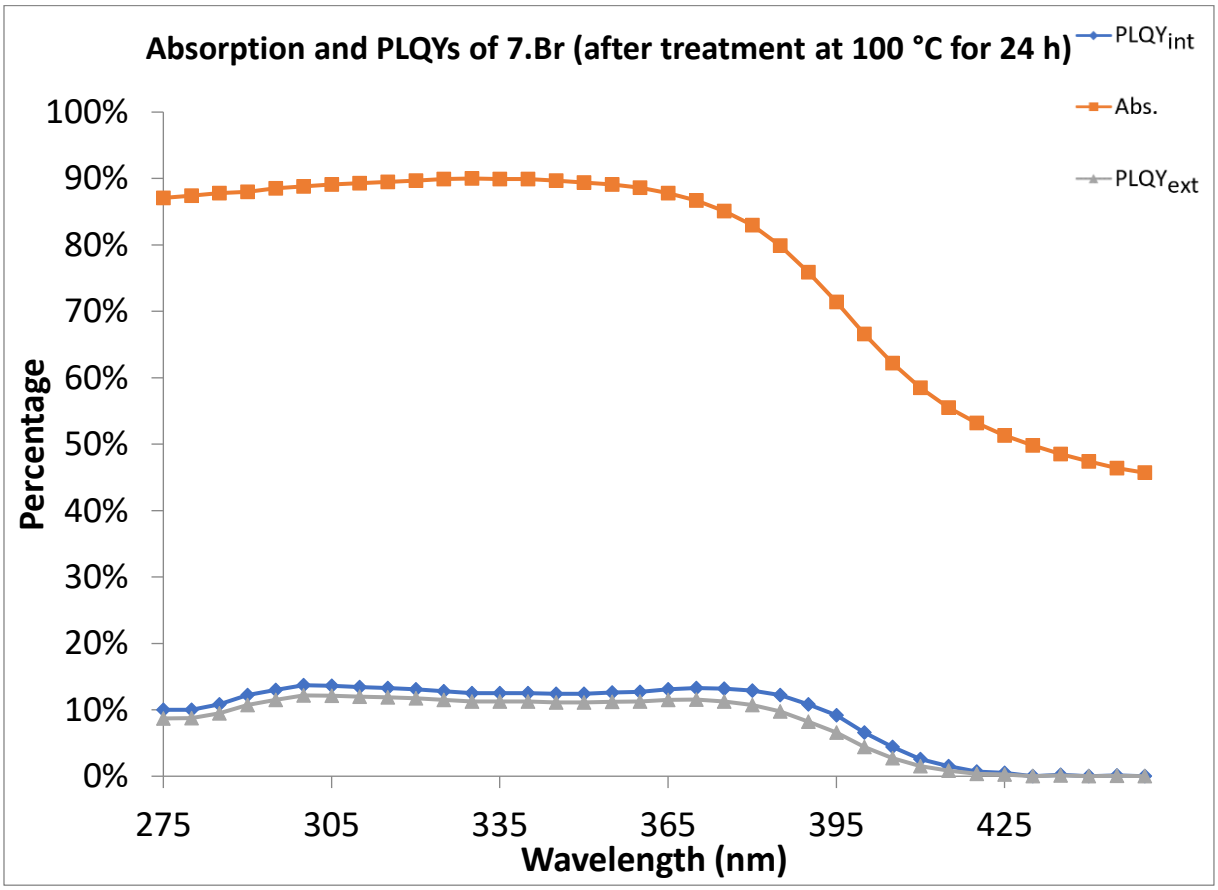


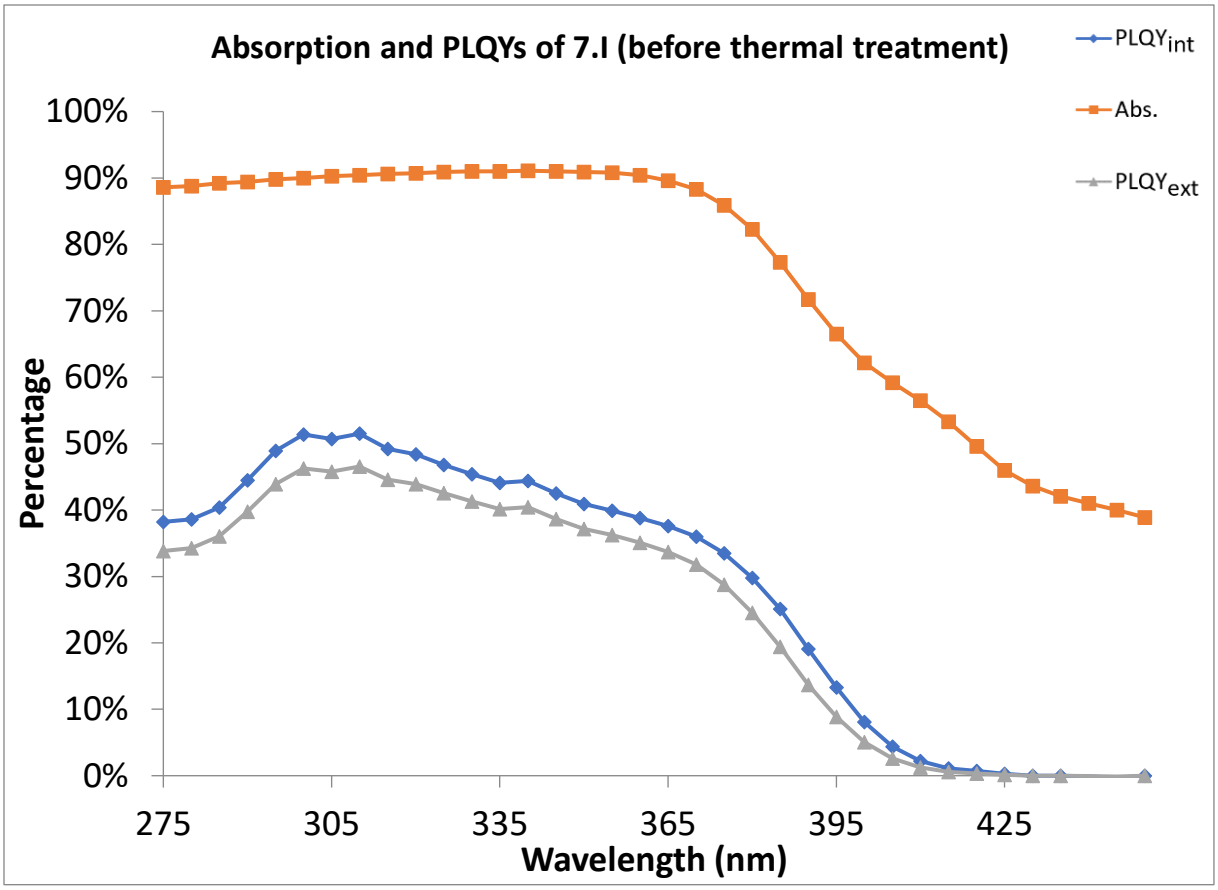
Fig. S4 CIE2015 diagram for the variation of halide/pseudohalide in the **7**.X series

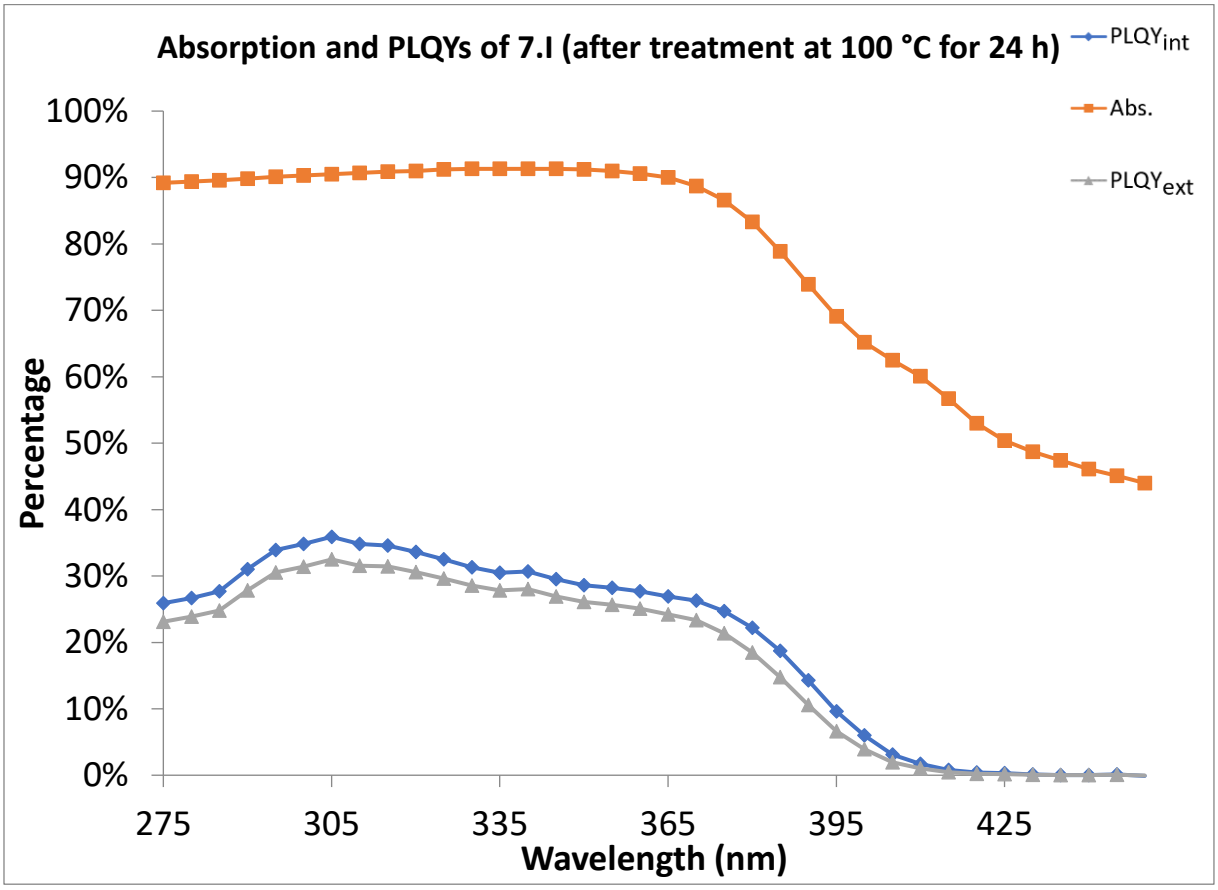

Absorption and PLQYs of 7.Cl (before thermal treatment)
PLQYint
Abs.
PLQYext
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Percentage
275
305
335
365
395
425
Wavelength (nm)

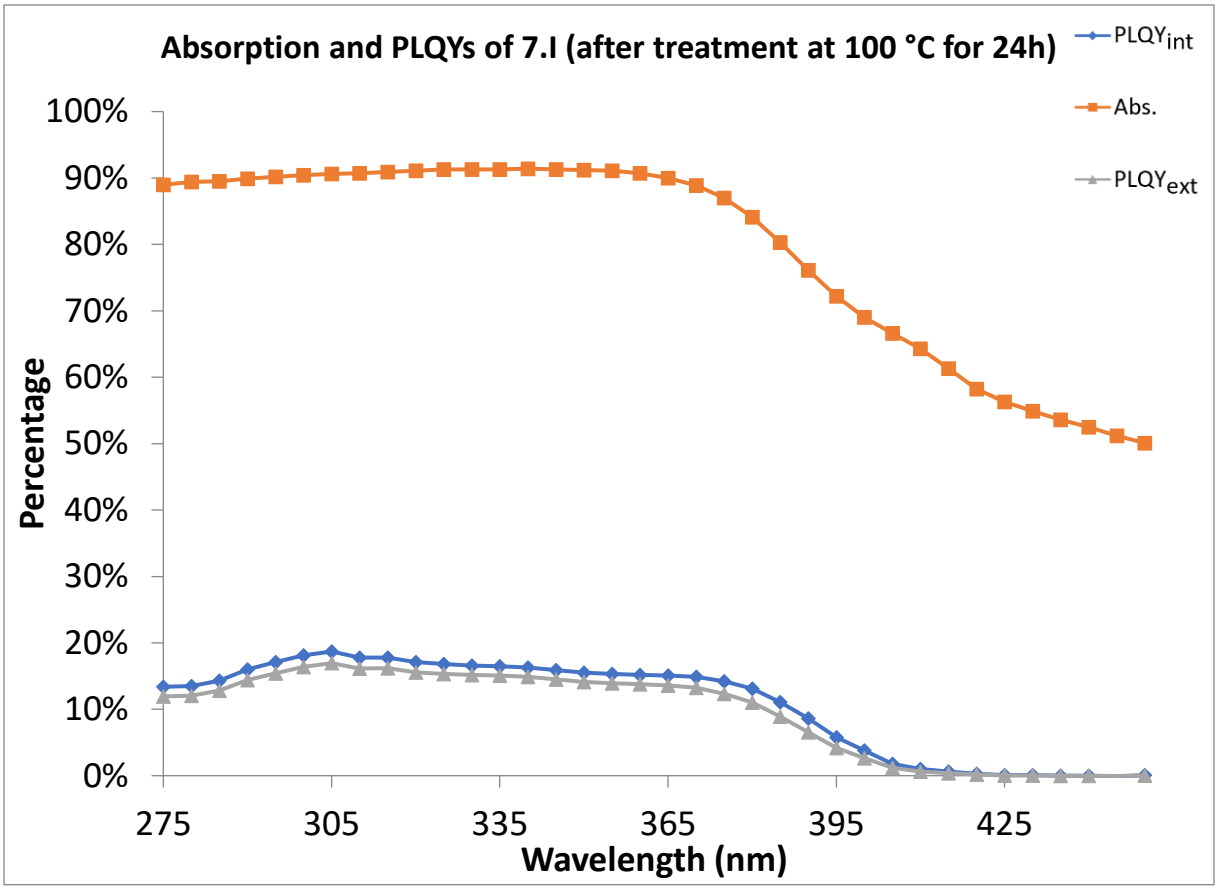

Absorption and PLQYs of 7.Cl (after treatment at 100 °C for 24 h)
PLQYint
Abs.
PLQYext
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Percentage
275
305
335
365
395
425
Wavelength (nm)

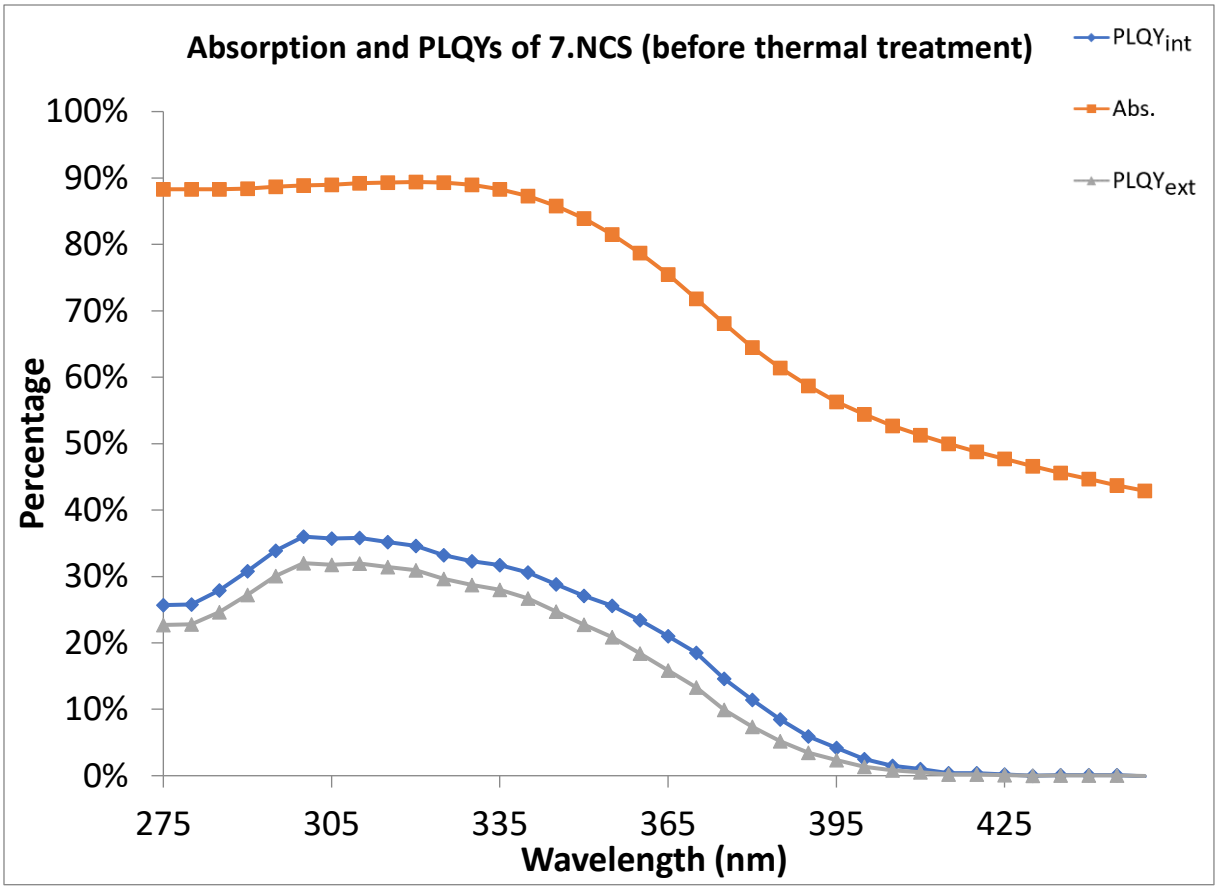

Absorption and PLQYs of 7.Br (before thermal treatment)
PLQYint
Abs.
PLQYext
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Percentage
275
305
335
365
395
425
Wavelength (nm)

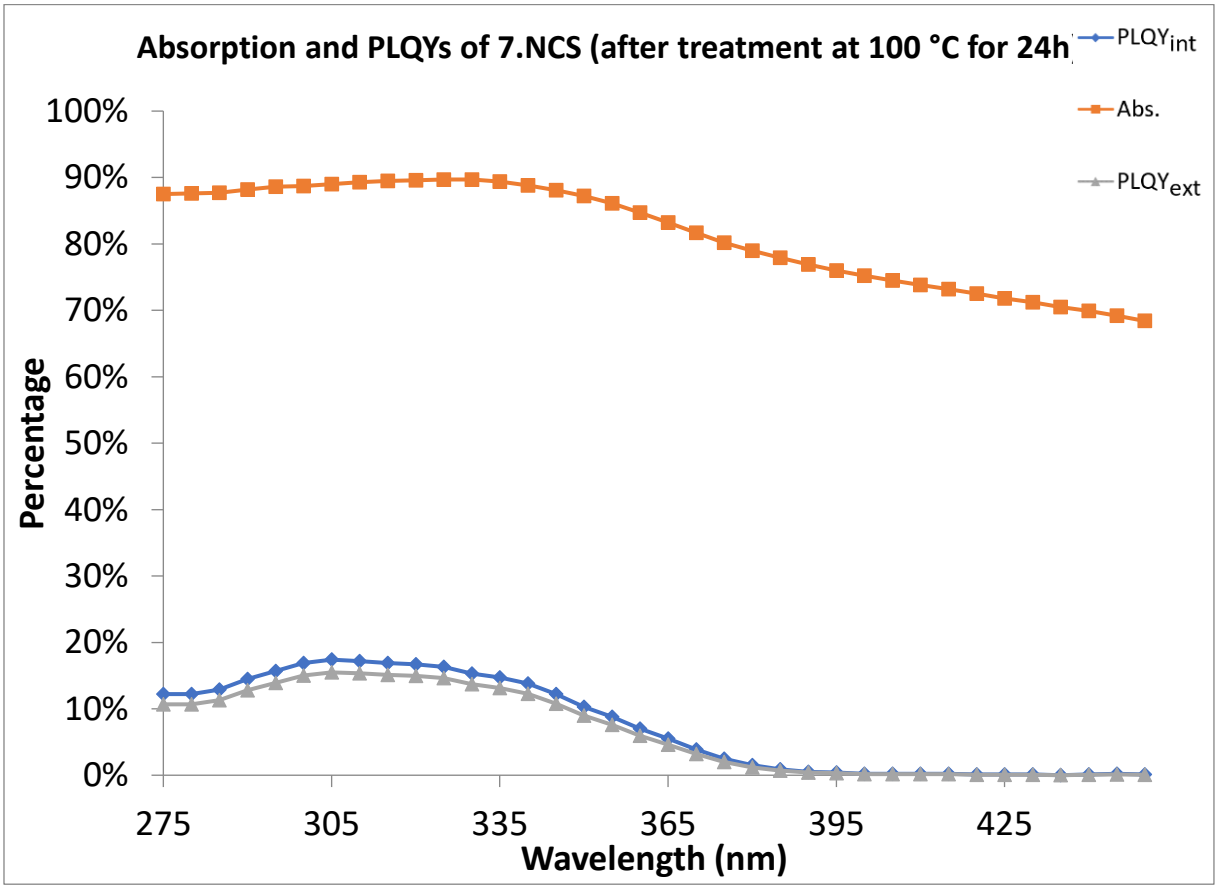

Absorption and PLQYs of 7.Br (after treatment at 100 °C for 24 h)
PLQYint
Abs.
PLQYext
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Percentage
275
305
335
365
395
425
Wavelength (nm)

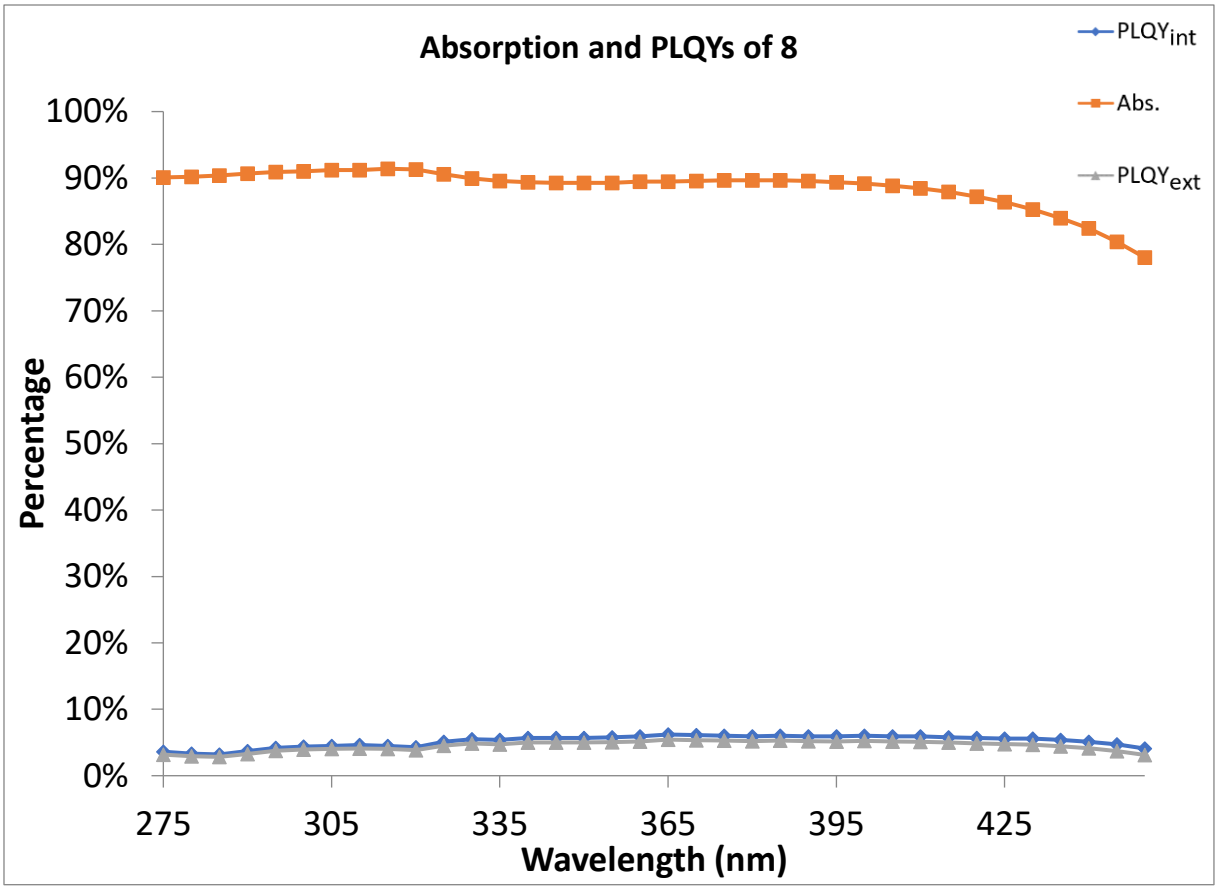

Absorption and PLQYs of 7.I (before thermal treatment)
PLQYint
Abs.
PLQYext
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Percentage
275
305
335
365
395
425
Wavelength (nm)

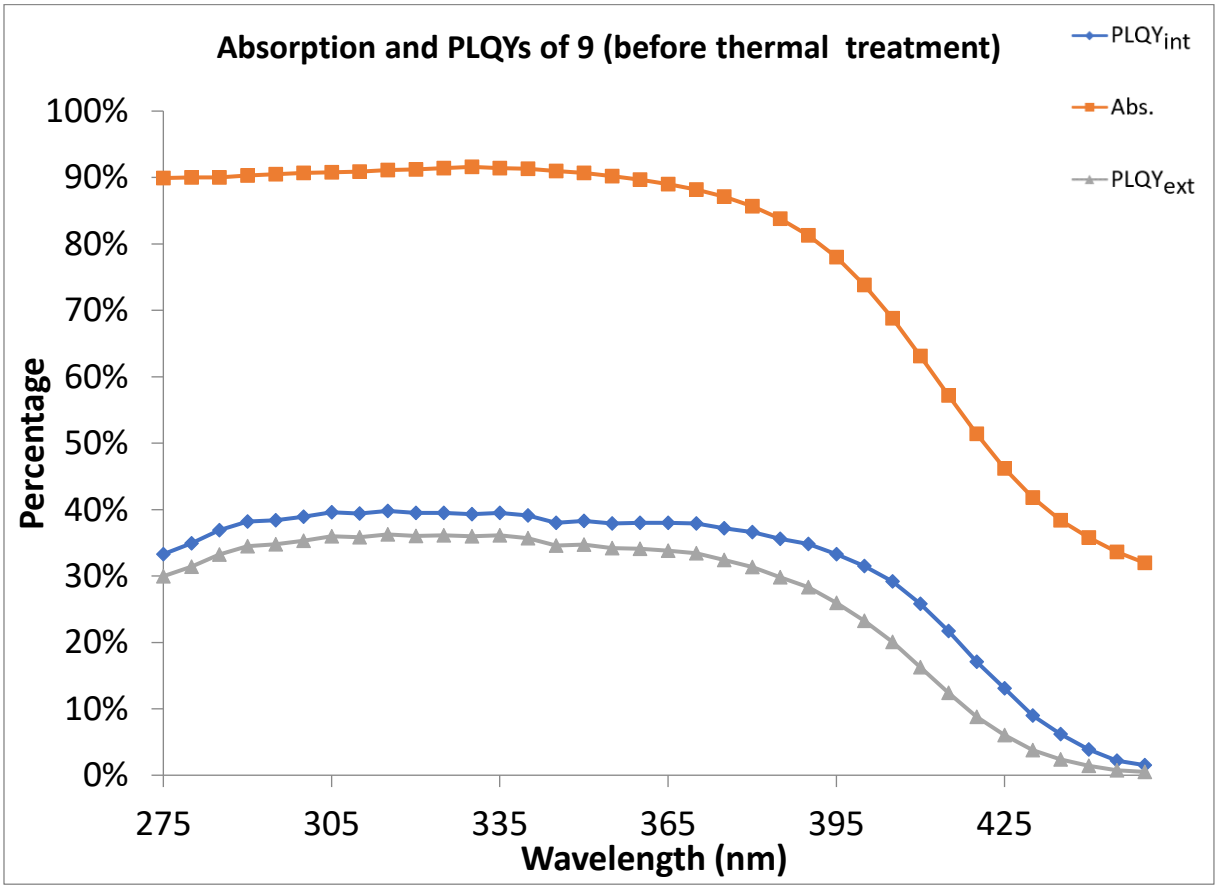

Absorption and PLQYs of 7.I (after treatment at 100 °C for 24 h)
PLQYint
Abs.
PLQYext
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Percentage
275
305
335
365
395
425
Wavelength (nm)


Absorption and PLQYs of 7.I (after treatment at 100 °C for 24h)
PLQYint
Abs.
PLQYext
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Percentage
275
305
335
365
395
425
Wavelength (nm)


Absorption and PLQYs of 7.NCS (before thermal treatment)
PLQYint
Abs.
PLQYext
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Percentage
275
305
335
365
395
425
Wavelength (nm)


Absorption and PLQYs of 7.NCS (after treatment at 100 °C for 24h
PLQYint
Abs.
PLQYext
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Percentage
275
305
335
365
395
425
Wavelength (nm)


Absorption and PLQYs of 8
PLQYint
Abs.
PLQYext
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Percentage
275
305
335
365
395
425
Wavelength (nm)


Absorption and PLQYs of 9 (before thermal treatment)
PLQYint
Abs.
PLQYext
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Percentage
275
305
335
365
395
425
Wavelength (nm)

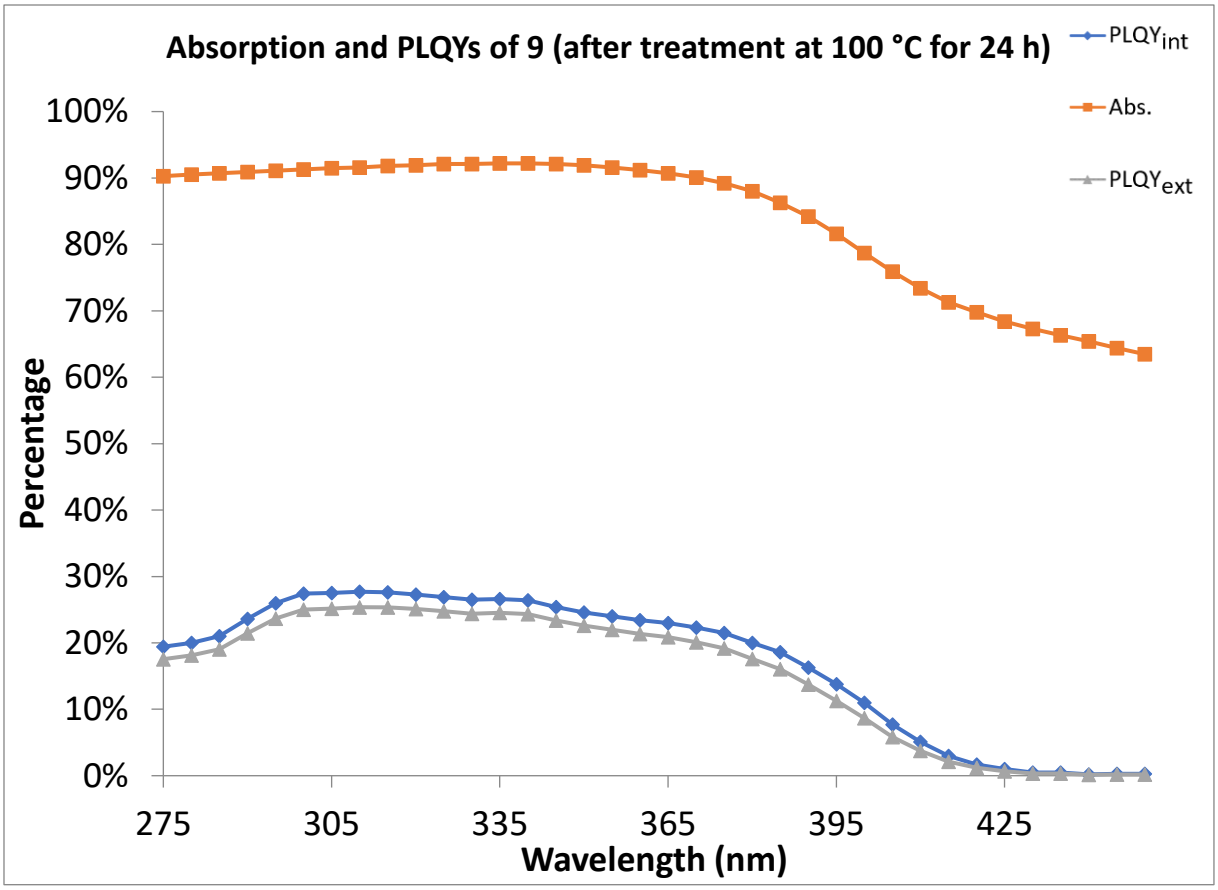


Fig. S5 Variation of PL QY_{ext} PL QY_{int} and Abs. as a function of the excitation wavelength at room temperature for complexes **7**.X (X = Cl, Br, NCS and I), 8, 9; after thermal treatment at 100 °C during 24 h (or 120 h) where relevant.

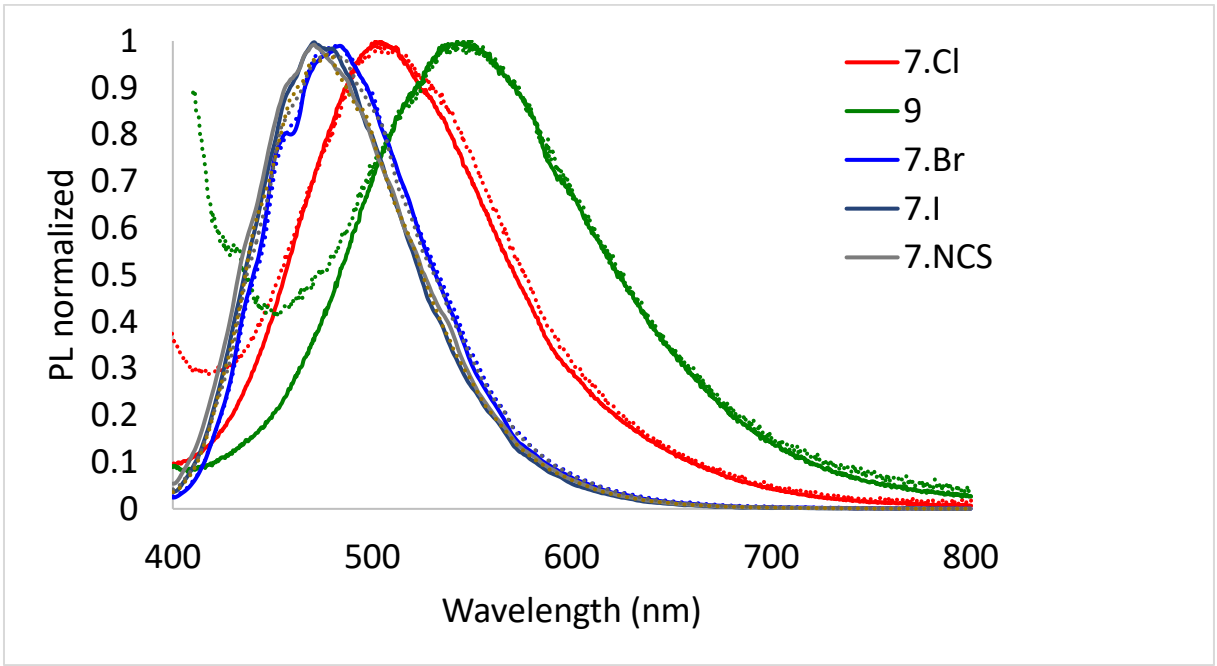
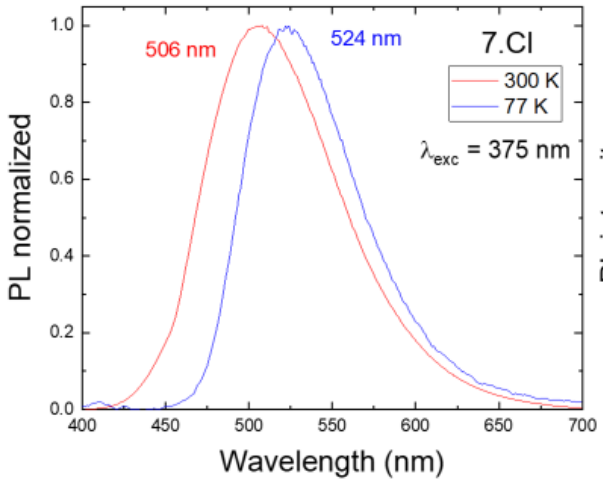
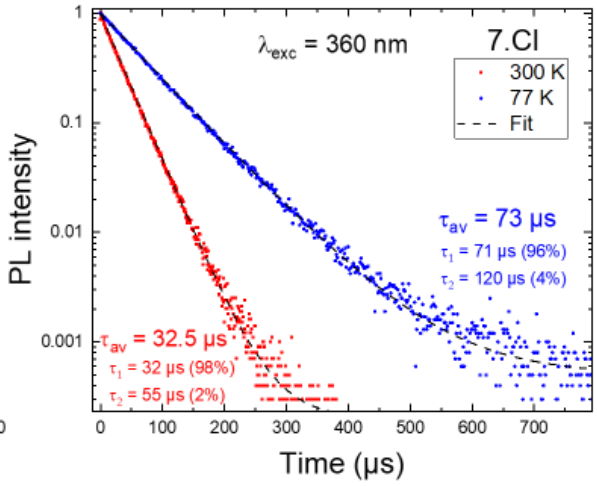
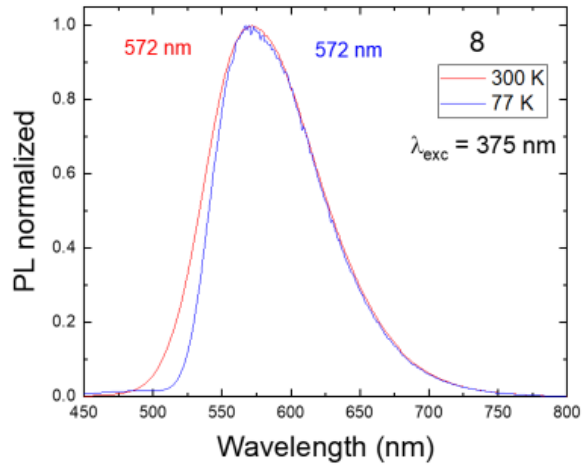
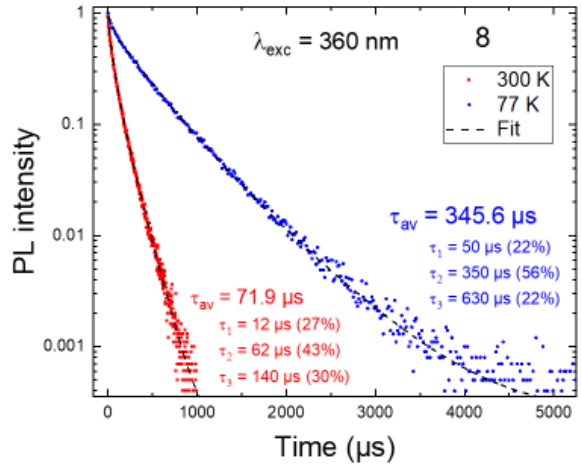


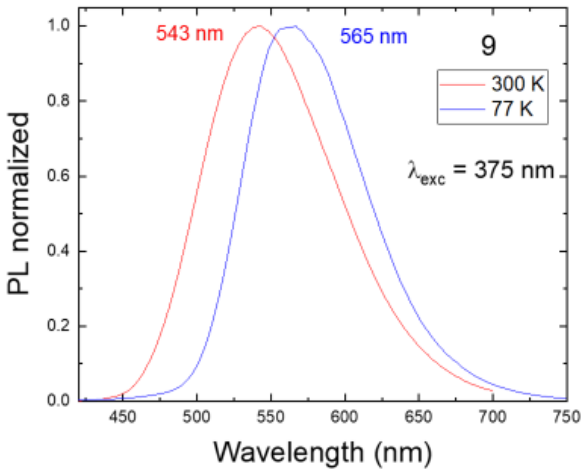
Fig. S6 Comparison of **7**.Cl, **9, 7**.Br**, 7.**NCS before and after thermal treatment (100°C, 24h). Emission spectra recorded with 331, 336, 330 and 331 as respective λ_{exc} values.

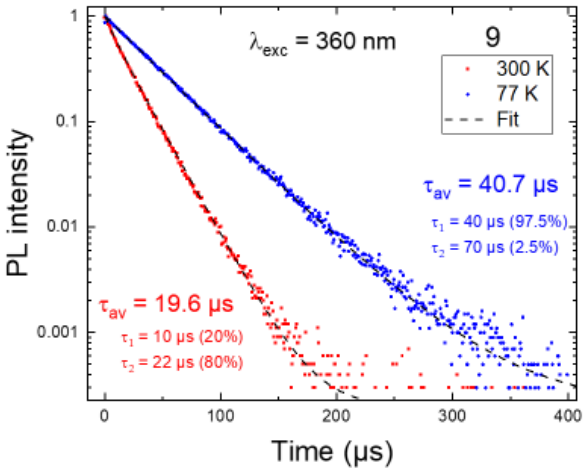

506 nm
524 nm
7.Cl
300 K
77 K
λexc = 375 nm
PL normalized
Wavelength (nm)

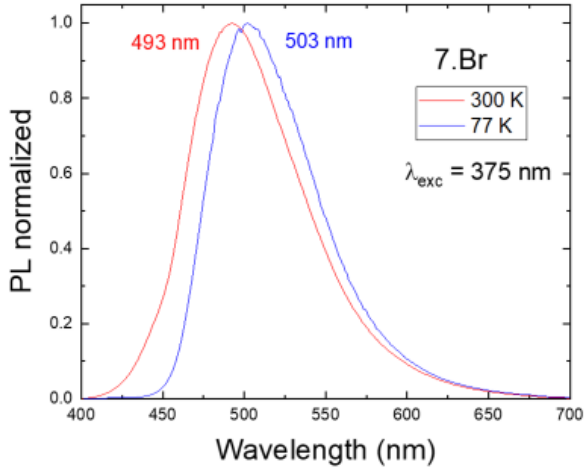

λexc = 360 nm
7.Cl
300 K
77 K
Fit
τav = 73 µs
τ1 = 71 µs (96%)
τ2 = 120 µs (4%)
τav = 32.5 µs
τ1 = 32 µs (98%)
τ2 = 55 µs (2%)
PL intensity
Time (µs)

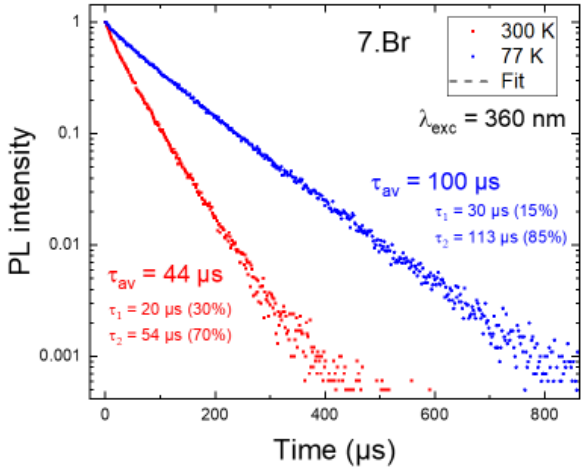

572 nm
572 nm
8
300 K
77 K
λexc = 375 nm
PL normalized
Wavelength (nm)

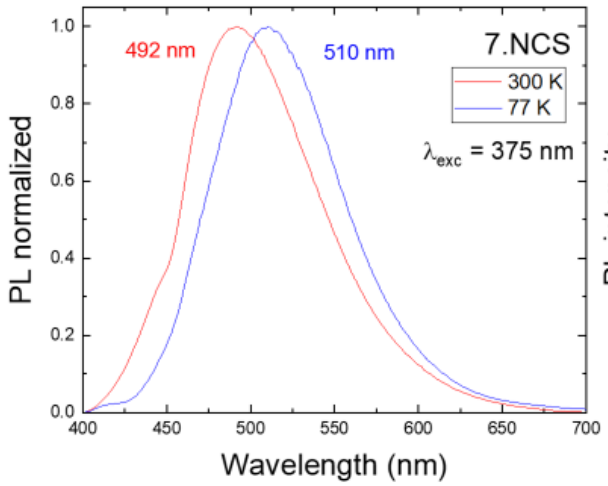

λexc = 360 nm
8
300 K
77 K
Fit
τav = 345.6 µs
τ1 = 50 µs (22%)
τ2 = 350 µs (56%)
τ3 = 630 µs (22%)
τav = 71.9 µs
τ1 = 12 µs (27%)
τ2 = 62 µs (43%)
τ3 = 140 µs (30%)
PL intensity
Time (µs)

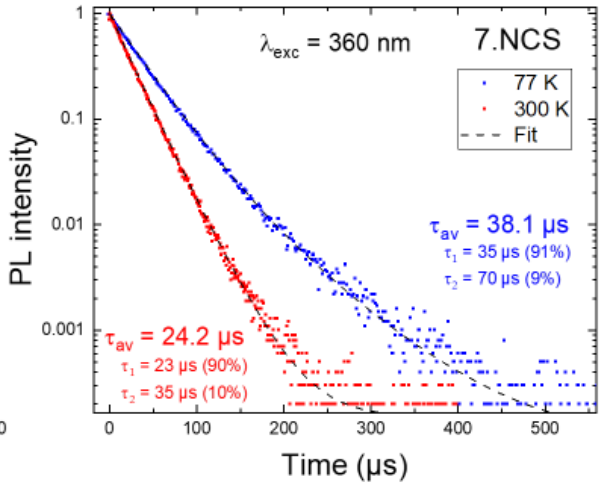

543 nm
565 nm
9
300 K
77 K
λexc = 375 nm
PL normalized
Wavelength (nm)

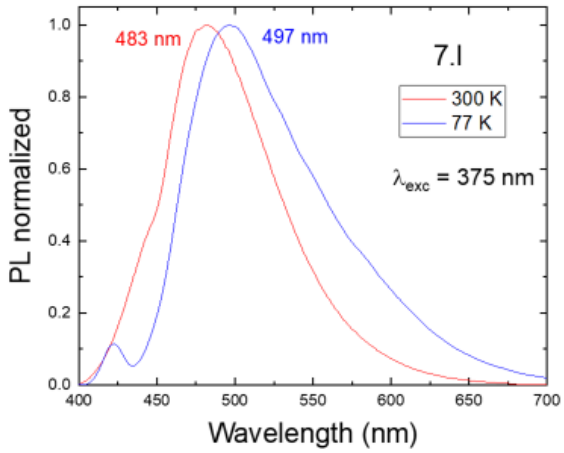

λexc = 360 nm
9
300 K
77 K
Fit
τav = 40.7 μs
τ1 = 40 μs (97.5%)
τ2 = 70 μs (2.5%)
τav = 19.6 μs
τ1 = 10 μs (20%)
τ2 = 22 μs (80%)
PL intensity
Time (μs)

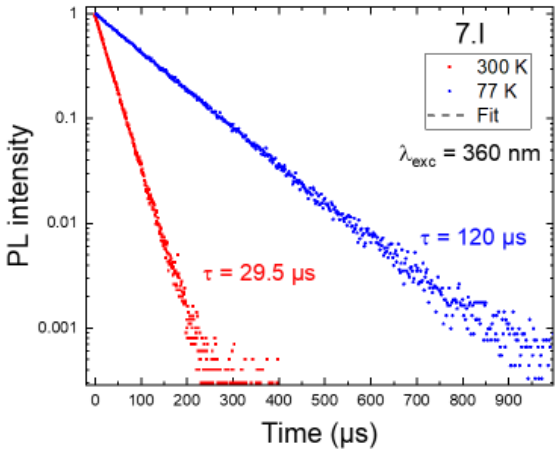

493 nm
503 nm
7.Br
300 K
77 K
λexc = 375 nm
PL normalized
Wavelength (nm)


7.Br
300 K
77 K
Fit
λexc = 360 nm
τav = 100 μs
τ1 = 30 μs (15%)
τ2 = 113 μs (85%)
τav = 44 μs
τ1 = 20 μs (30%)
τ2 = 54 μs (70%)
PL intensity
Time (μs)


492 nm
510 nm
7.NCS
300 K
77 K
λexc = 375 nm
PL normalized
Wavelength (nm)


λexc = 360 nm
7.NCS
77 K
300 K
Fit
τav = 38.1 μs
τ1 = 35 μs (91%)
τ2 = 70 μs (9%)
τav = 24.2 μs
τ1 = 23 μs (90%)
τ2 = 35 μs (10%)
PL intensity
Time (μs)


483 nm
497 nm
7.I
300 K
77 K
λexc = 375 nm
PL normalized
Wavelength (nm)


7.I
300 K
77 K
Fit
λexc = 360 nm
τ = 120 μs
τ = 29.5 μs
PL intensity
Time (μs)

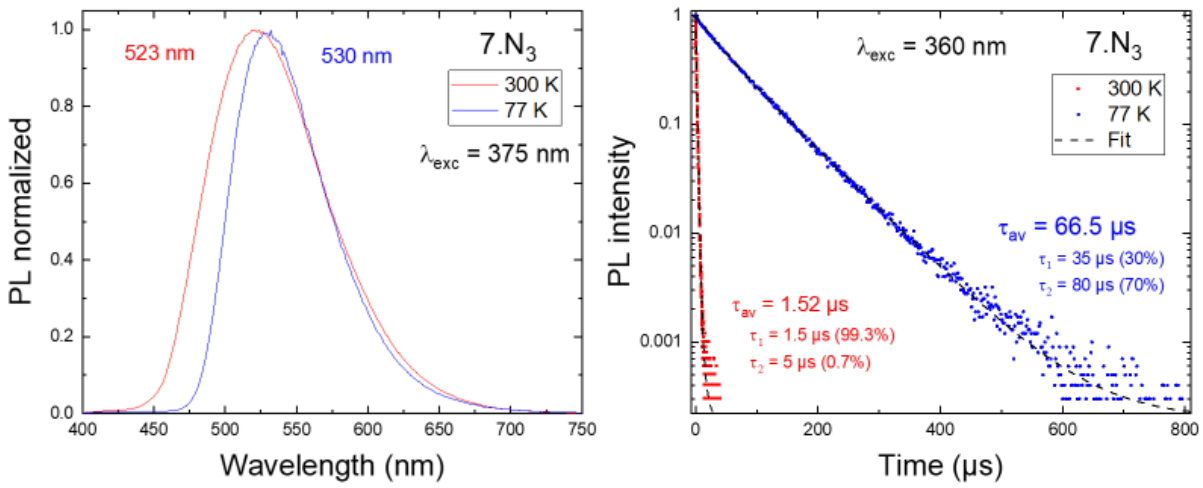


Fig. S7 left) emission spectra at room temperature and 77K (λ_{exc} = 375 nm); right) luminescence decay profiles at room temperature and 77 K (λ_{exc} = 360 nm, λ_{em} detailed in Table 3), of the powders **7**.X (X = Cl, Br, NCS, I, N_3), **8** and **9**.