Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supporting Information

Tunable dual-emission luminescence from Cu (I)-cluster-based MOFs for multi-stimuli responsive materials

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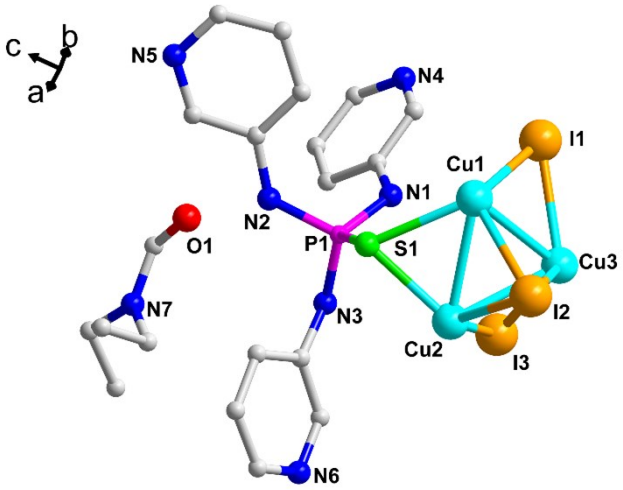


Figure S1. Asymmetric unit of **1**.

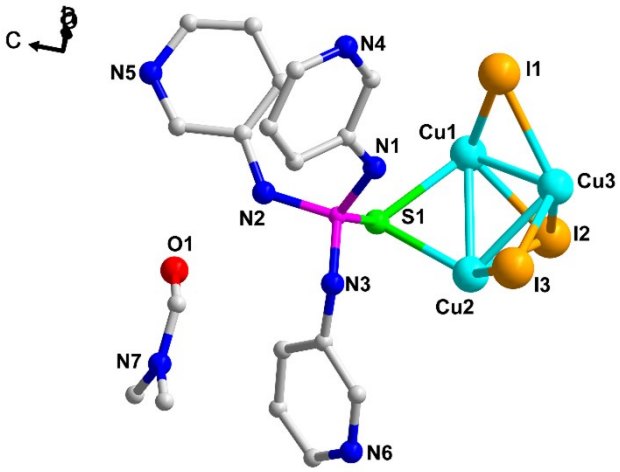


Figure S2. Asymmetric unit of **2**.

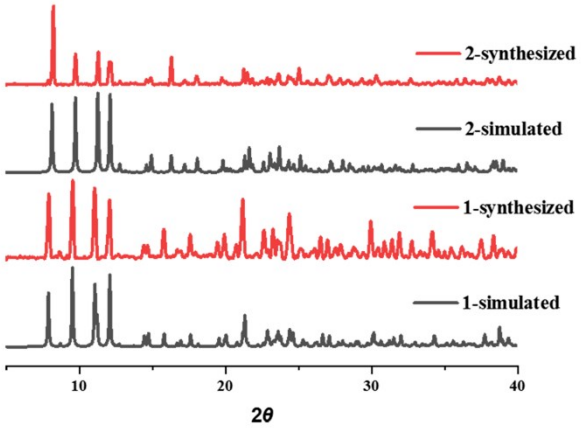


Figure S3. PXRD patterns of the compounds.

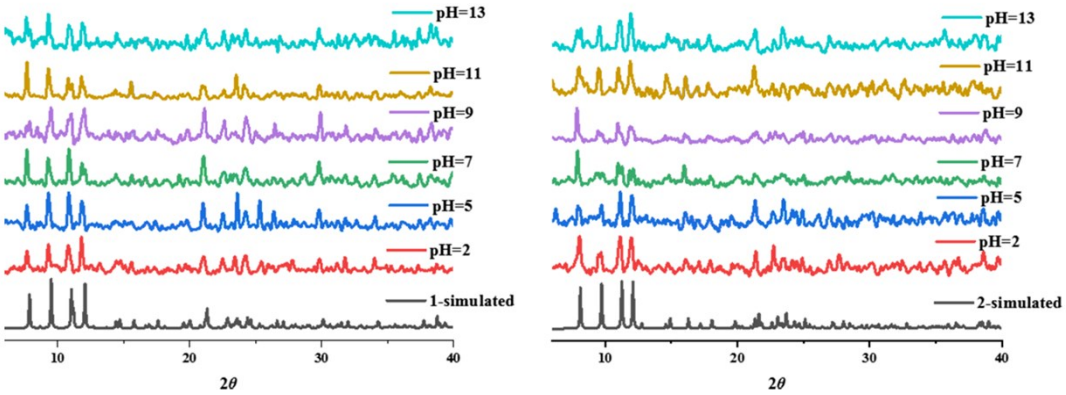


Figure S4. PXRD patterns of **1** (left) and **2** (right) after immersed in different pH of aqueous solutions.

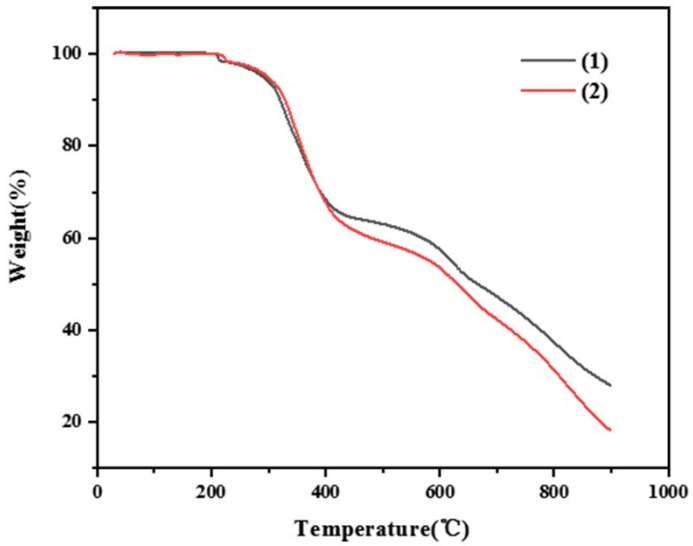


Figure S5. TG curves of compounds **1** and **2**.

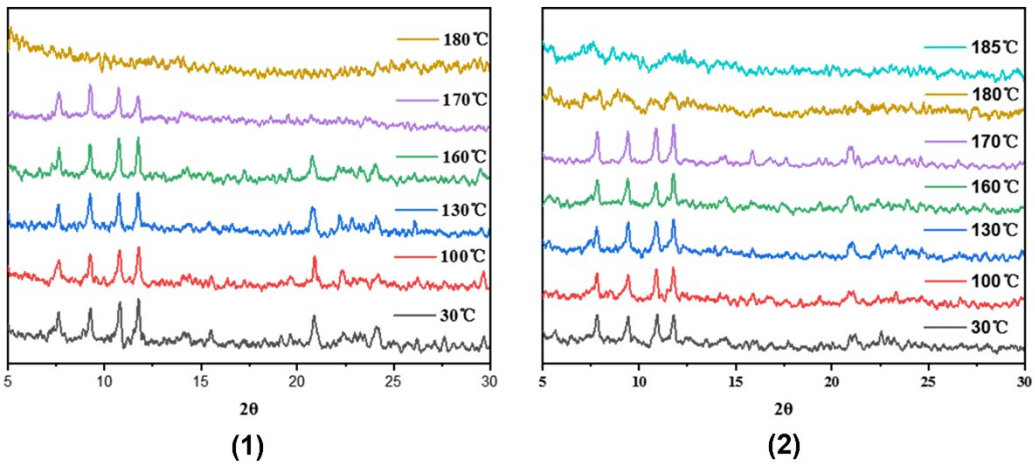


Figure S6. Temperature-dependent PXRD patterns of **1** (left) and **2** (right).

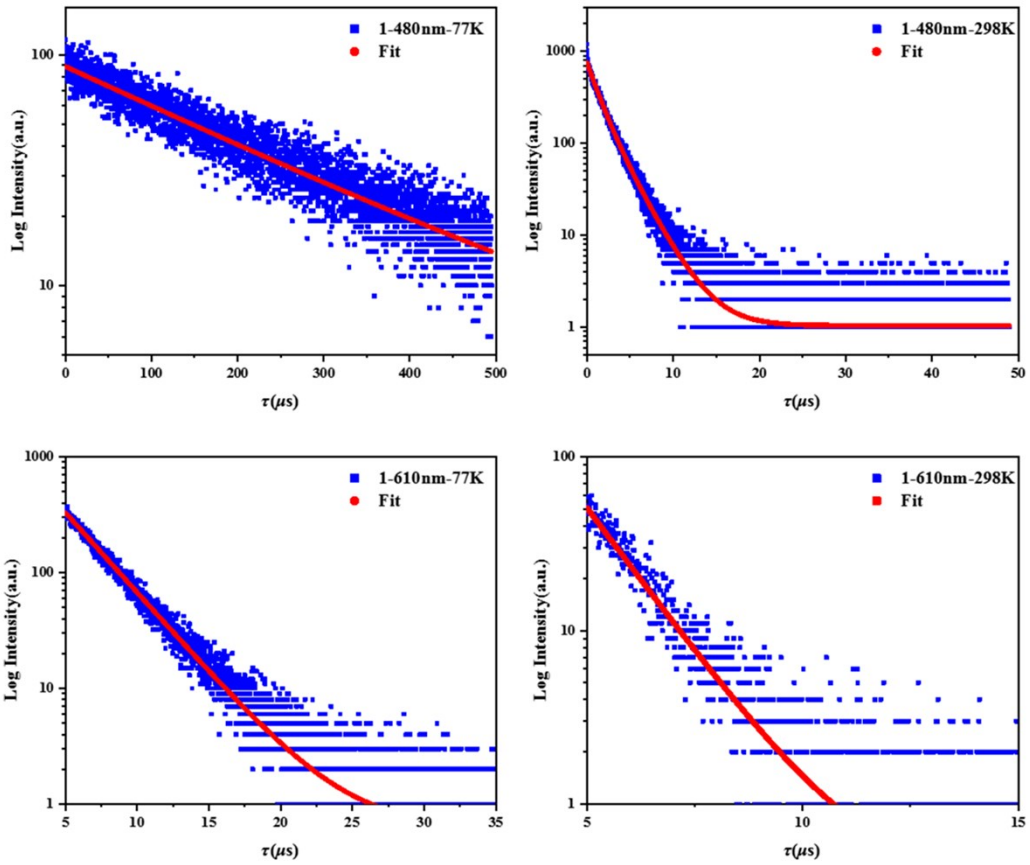


Figure S7. Lifetimes of **1** excited at 379 nm at 77 K and 298 K.

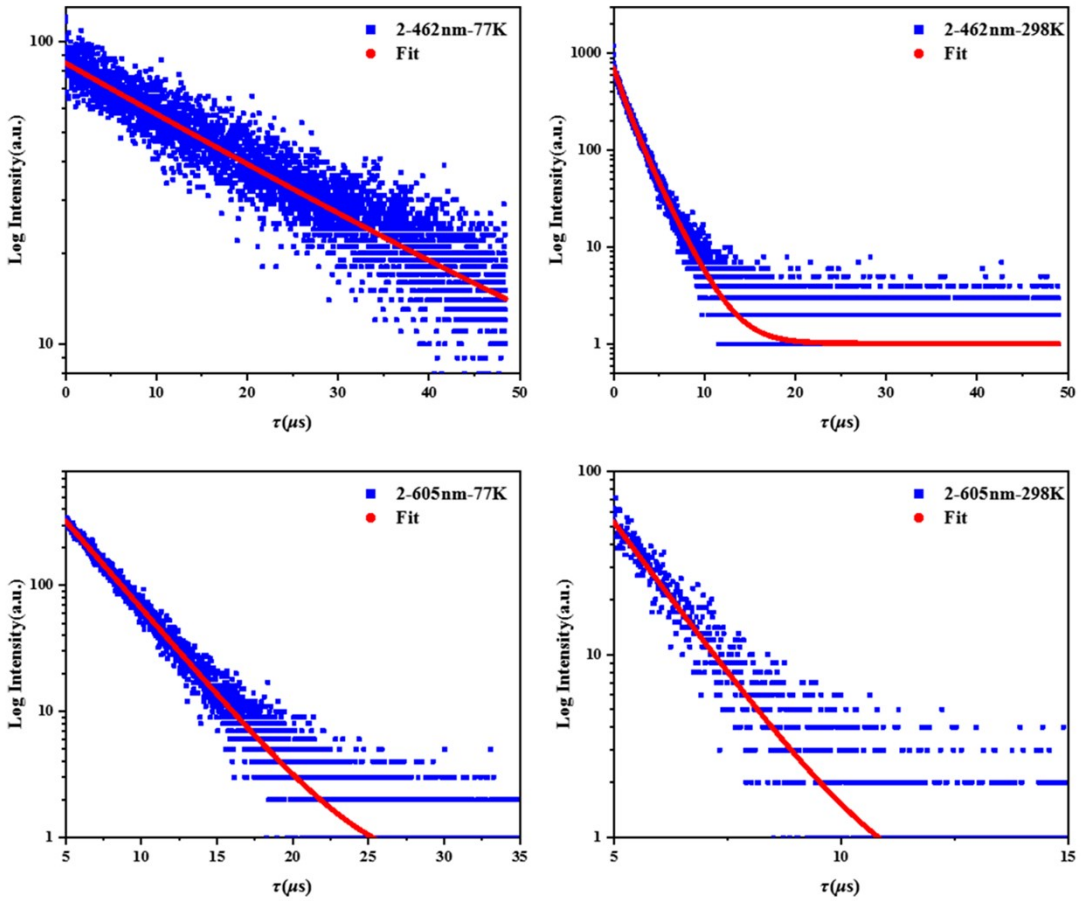


Figure S8. Lifetimes of **2** excited at 370 nm at 77 K and 298 K.

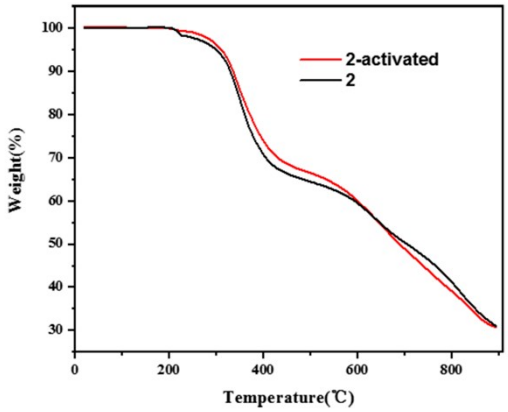


Figure S9. The TG curves of **2** and **2**-activated after activation.

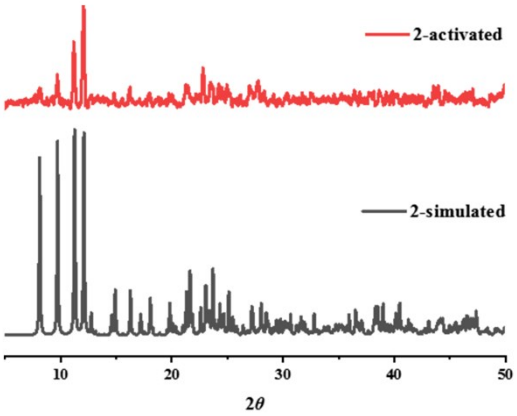


Figure S10. The experimental PXRD pattern for activated samples and simulated pattern.

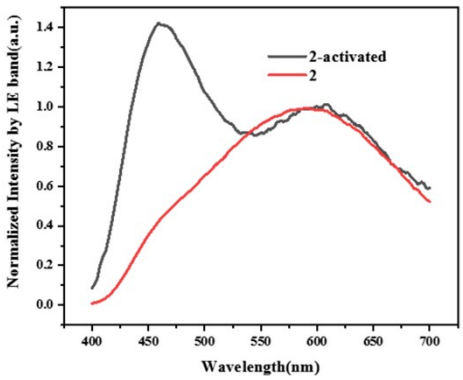


Figure S11. The emission spectra of **2** and **2**-activated normalized by LE-band intensity.

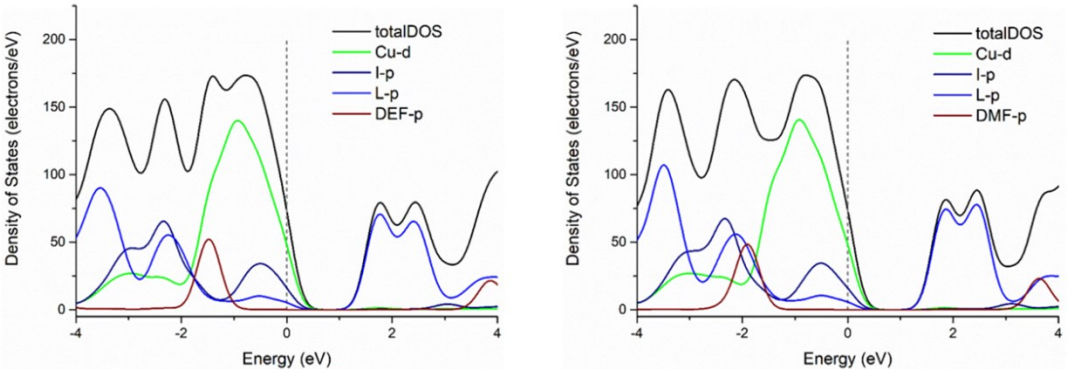


Figure S12. DOS analyses of the two compounds.

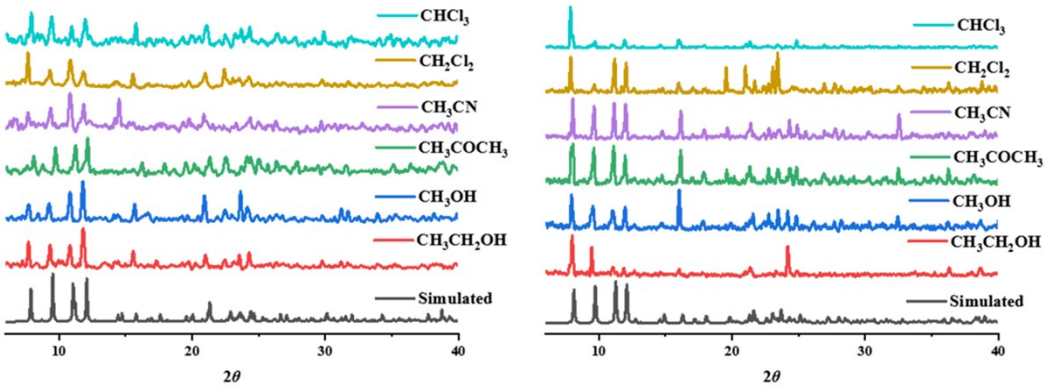


Figure S13. PXRD patterns of **1** (left) and **2** (right) after immersed in different solvents.

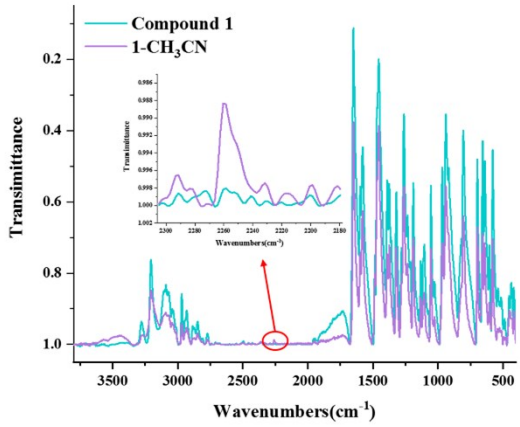


Figure S14. The IR spectra of **1** and **1**-CH_3CN.

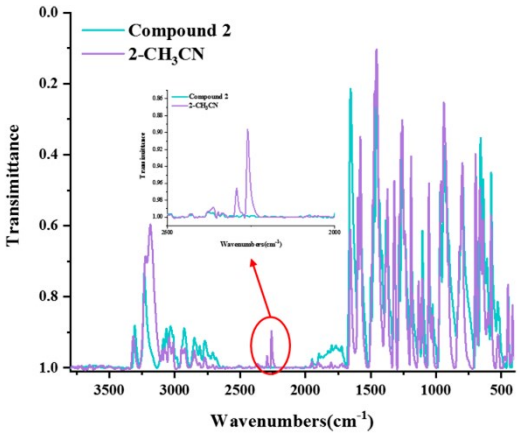


Figure S15. The IR spectra of **2** and **2**-CH_3CN.

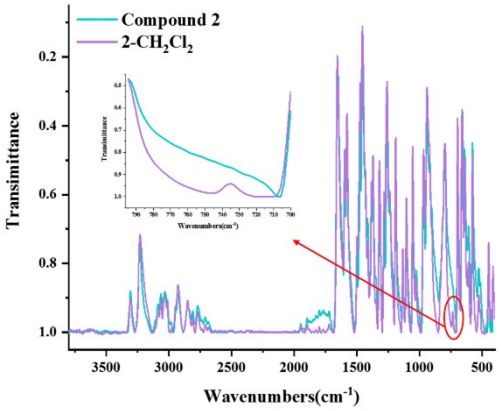


Figure S16. The IR spectra of **2** and **2**-CH_2Cl_2.

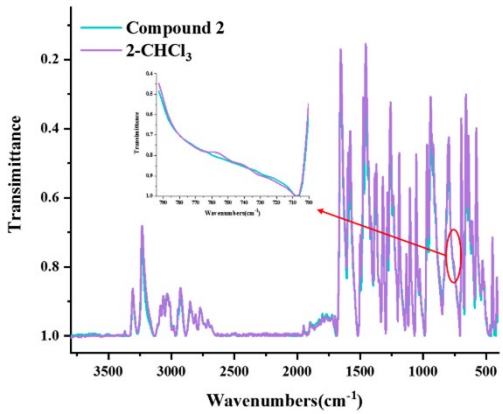


Figure S17. The IR spectra of **2** and **2**-$CHCl_3$.

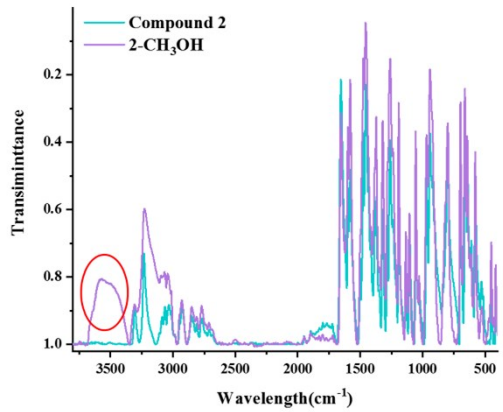


Figure S18. The IR spectra of **2** and **2**-CH_3OH.

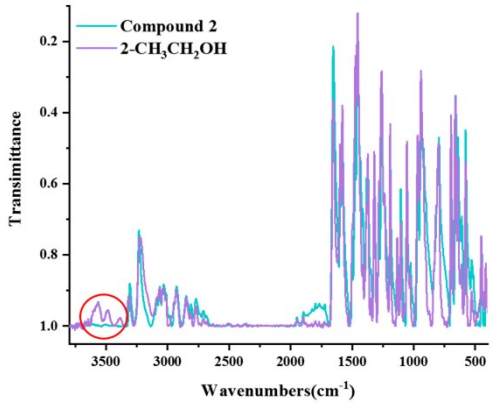


Figure S19. The IR spectra of **2** and **2**-CH_3CH_2OH.

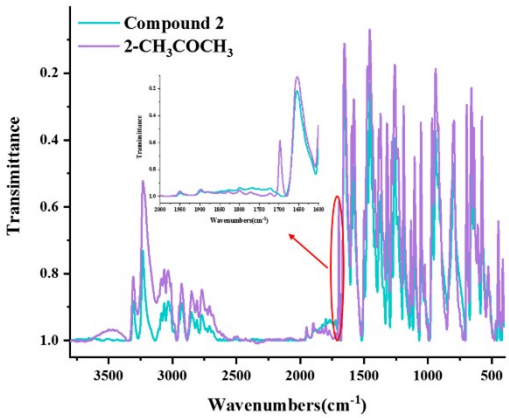


Figure S20. The IR spectra of **2** and **2**-CH_3COCH_3.

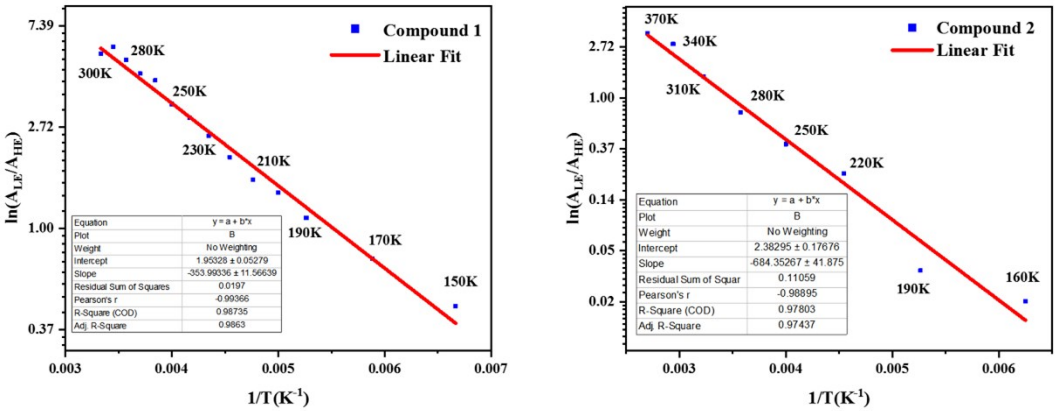


Figure S21. The linear curves between the area of two emission bands and 1/T of two compounds: **1** (left) and **2** (right).

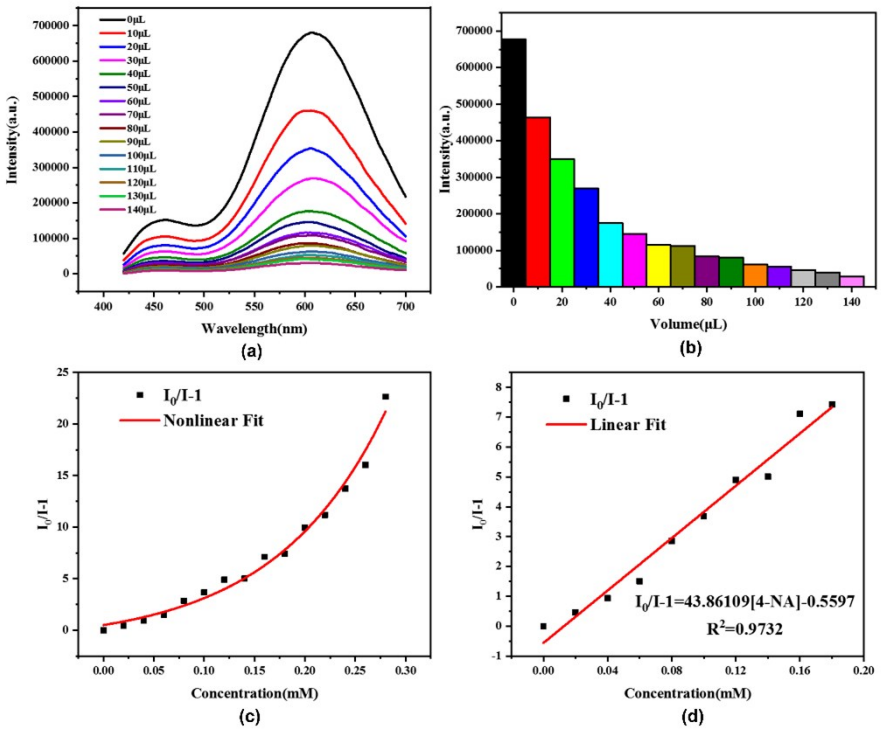


Figure S22. (a) PL spectra of Compound **1** in 4-NA. (b) The intensity of emission band at 610 nm with 4-NA adding. (c) Nonlinear relationship between I_0 and I. (d) Linear relationship between I_0 and I at low concentration.

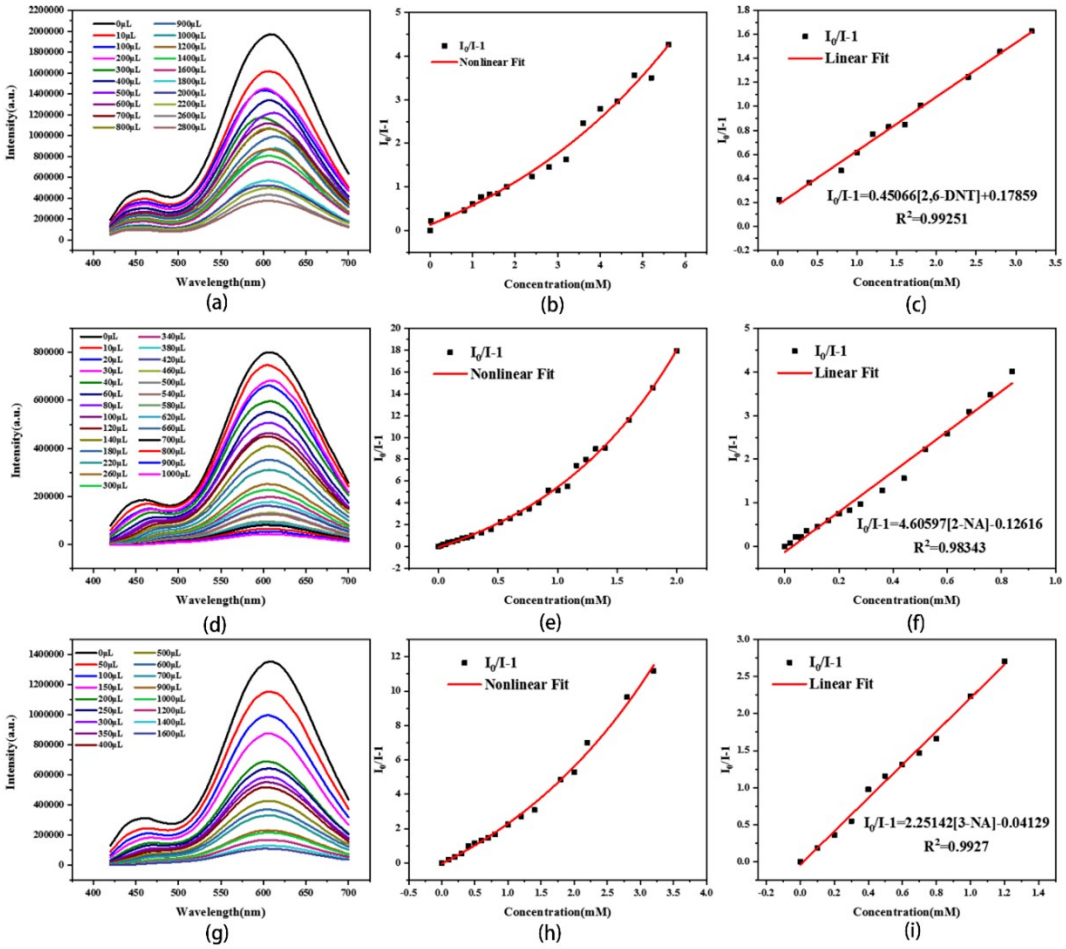


Figure S23. PL spectra and linearly fitted curves of compound **1** in 2, 6-DNT, 2-NA, 3-NA.

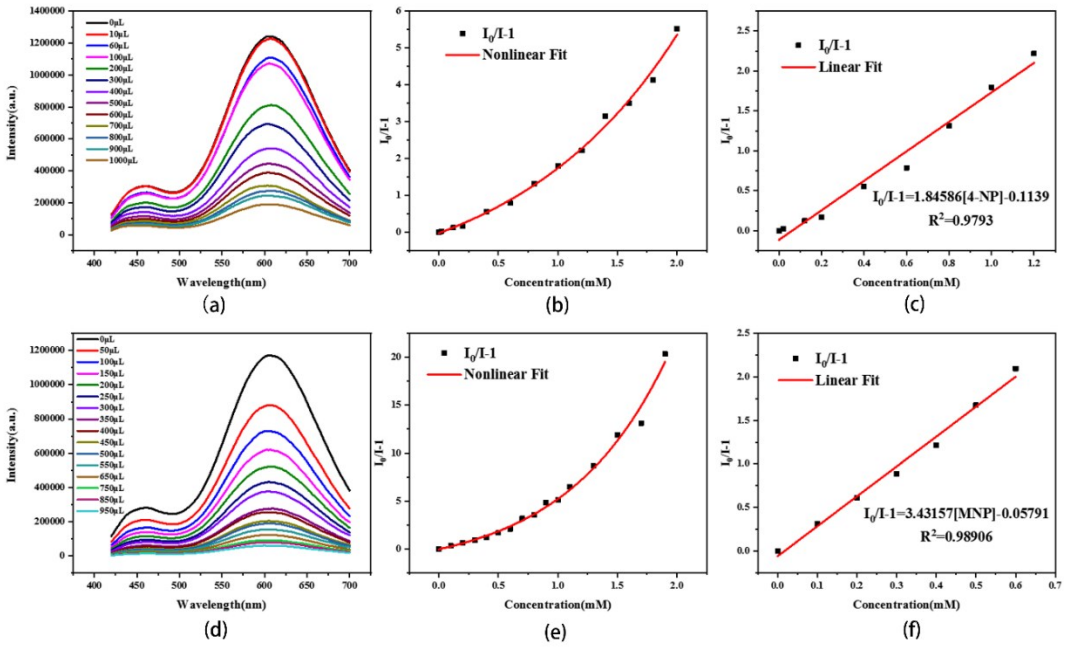


Figure S24. PL spectra and linearly fitted curves of compound **1** in 4-NP and MNP.

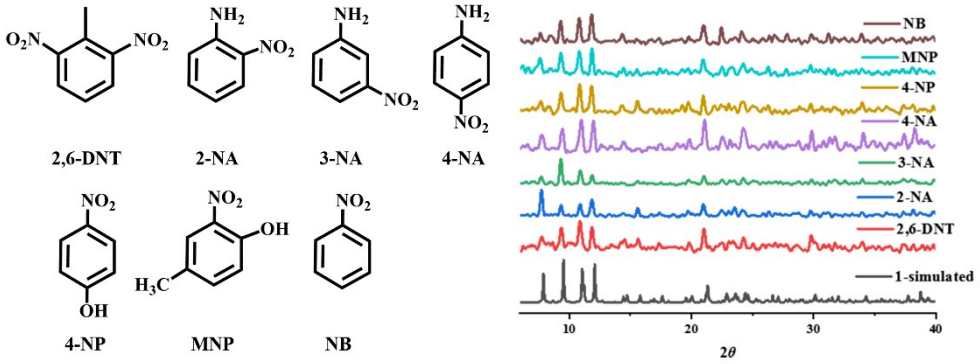


Figure S25. Different nitro-compounds and PXRD patterns of **1** after immersed

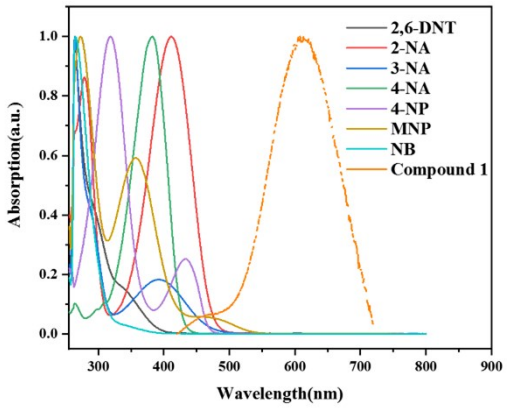
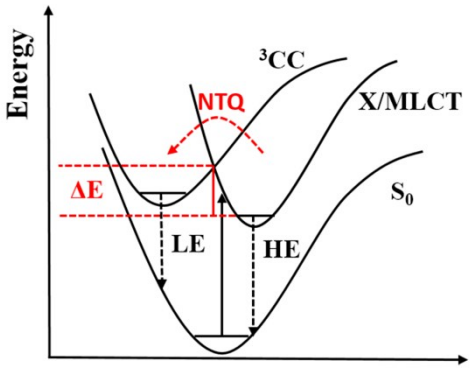


Figure S26. Spectral overlaps of the emission spectra of **1** with the UV-vis spectra of different nitro-compounds.

Supplementary Scheme



Scheme. S1 Illustration of NTQ induced by the energy transfer from X/MLCT and ^{3}CC states.

Supplementary Tables

Table S1. Crystal data collection and structure refinement parameters.

Compound 1	**1(100 K)**	**1(200 K)**	**1(298 K)**
Empirical formula	$C_{20}H_{26}Cu_3I_3N_7OPS$	$C_{20}H_{26}Cu_3I_3N_7OPS$	$C_{20}H_{26}Cu_3I_3N_7OPS$
Formula weight	1014.83	1014.83	1014.83
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Pbca*	*Pbca*	*Pbca*
***a*/Å**	16.53192	16.5787(3)	16.6113(3)
***b*/Å**	15.77722	15.88552	15.9932(4)
***c*/Å**	22.4311(3)	22.4738(4)	22.5054(5)
***α*/°**	90	90	90
***β*/°**	90	90	90
***γ*/°**	90	90	90

Volume/Å^3	5850.64(13)	5918.72(17)	5979.02
Z	8	8	8
ρ_{calc} g/cm^3	2.304	2.278	2.255
μ/mm^{-1}	28.809	28.478	28.191
F(000)	3840.0	3840.0	3840.0
GOOF	1.043	1.020	1.038
R_{int}	0.0534	0.0336	0.0341
R_1	0.0405	0.0333	0.0318
ωR_2	0.0946	0.0710	0.0760
Compound 2	**2(100K)**	**2(200K)**	**2(298K)**
Empirical formula	$C_{18}H_{22}Cu_3I_3N_7OPS$	$C_{18}H_{22}Cu_3I_3N_7OPS$	$C_{18}H_{22}Cu_3I_3N_7OPS$
Formula weight	986.77	986.77	986.77
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Pbca*	*Pbca*	*Pbca*
***a*/Å**	16.55536(19)	16.5966(3)	16.6231(4)
***b*/Å**	15.68341(18)	15.7587(3)	15.8506(4)
***c*/Å**	21.7743(3)	21.8393(4)	21.9202(5)
***α*/°**	90	90	90
***β*/°**	90	90	90
***γ*/°**	90	90	90
Volume/Å^3	5653.58(11)	5711.87(18)	5775.72

Z	8	8	8
ρ_{calc} g/cm^3	2.319	2.295	2.270
μ/mm^{-1}	29.788	29.48	29.16
F(000)	3712.0	3712.0	3712.0
GOOF	1.051	1.0230	1.0280
R_{int}	0.0348	0.0441	0.0331
R_1	0.0248	0.0274	0.0262
ωR_2	0.0561	0.0660	0.0599

Table S2. Lifetimes of compounds.

Compound	Emission band	Total-lifetime-298 K (μs)	Lifetime-(μs)	%
1	480nm	0.20	0.13	43.27%
			0.26	56.73%
	610nm	12.98	12.98	100%
2	462nm	0.19	0.11	29.37%
			0.23	70.63%
	605nm	13.00	13.00	100%
Compound	**Emission band**	**Total-lifetime-77 K(μs)**	**Lifetime-(μs)**	**%**
1	480nm	24.54	24.54	100%
	610nm	31.31	31.31	100%
2	462nm	24.95	24.95	100%
	605nm	31.28	31.28	100%

Table S3. HOMO and LUMO energies of **1** and nitro-compounds calculated by Gaussian.

		HOMO (eV)	LUMO (eV)	Band Gap (eV)
MOF	1	+1.5793	-0.0001	1.5794
	2-NA	-6.4117	-2.8372	3.5745
	3-NA	-6.2374	-2.9002	3.3372

Analytes	4-NA	-6.4644	-2.5719	3.8925
	NB	-7.5912	-2.4283	5.1629
	2,6-DNT	-7.011	-2.125	4.886
	4-NP	-7.3519	-2.9904	4.3615
	MNP	-6.9872	-3.3656	3.6216

Bond	**100 K (Å)**	**200 K (Å)**	**298 K (Å)**
I2-Cu2	2.6816(8)	2.6902(7)	2.6975(9)
I2-Cu3	2.7603(9)	2.7650(7)	2.7681(10)
I2-Cu1	2.6503(8)	2.6517(7)	2.6524(9)
I1-Cu3	2.6748(9)	2.6817(8)	2.6902(10)
I1-Cu1	2.5777(9)	2.5789(7)	2.5790(9)
I3-Cu2	2.6397(8)	2.6474(7)	2.6514(9)
I3-Cu3	2.6874(9)	2.6902(8)	2.6923(10)
Cu2 -Cu3	2.6446(11)	2.6668(9)	2.6899(12)
Cu2 -Cu1	2.7516(11)	2.7800(9)	2.8100(12)
Cu2-S1	2.3946(14)	2.3937(11)	2.3997(14)
Cu2-N4[1]	2.059(4)	2.053(3)	2.061(4)
Cu1-Cu3	2.6769(11)	2.6977(9)	2.7246(12)
Cu3-N5[3]	2.062(4)	2.060(4)	2.071(4)
Cu1-S1	2.5054(15)	2.5099(12)	2.5228(16)
Cu1-N6[2]	2.046(4)	2.052(4)	2.050(4)
Symmetry codes: [1]1/2+X,+Y,1/2-Z; [2]3/2-X,-1/2+Y,+Z; [3]+X,1/2-Y,-1/2+Z.			

Table S4. Primary bond lengths of **1** at 100 K, 200 K, 298 K.

Table S5. Primary bond lengths of **2** at 100 K, 200 K, 298 K.

Bond	**100 K(Å)**	**200 K(Å)**	**298 K(Å)**
I3-Cu2	2.6221(5)	2.6283(7)	2.6324(7)
I3-Cu3	2.6729(5)	2.6758(7)	2.6783(8)
I2-Cu1	2.6376(5)	2.6411(8)	2.6450(8)
I2-Cu2	2.6867(5)	2.6948(7)	2.7008(7)
I2-Cu3	2.7835(5)	2.7890(8)	2.7912(8)
I1-Cu1	2.5818(5)	2.5827(8)	2.5797(7)
I1-Cu3	2.6879(5)	2.6944(8)	2.7033(8)
Cu1-Cu2	2.7713(7)	2.8037(10)	2.8438(10)
Cu1-Cu3	2.5982(7)	2.6191(9)	2.6442(10)
Cu1-S1	2.4894(9)	2.5063(12)	2.5249(13)
Cu1-N6[1]	2.040(3)	2.048(3)	2.048(3)
Cu2-Cu3	2.6657(7)	2.6828(10)	2.6961(10)

Cu2-S1	2.3401(8)	2.3449(11)	2.3545(12)
Cu2-N4[2]	2.049(3)	2.054(4)	2.054(3)
Cu3-N5[3]	2.045(3)	2.049(4)	2.052(3)
Symmetry codes: [1]1/2-X,1/2+Y,+Z; [2]-1/2+X,+Y,1/2-Z; [3]+X,3/2-Y,-1/2+Z.			

Table S6. Bond angles of **1** at 100 K, 200 K, 298 K.

Atom 1	Atom 2	Atom 3	Angle-100 K(˚)	Angle-200 K(˚)	Angle-298 K(˚)
Cu2	I3	Cu3	59.52(3)	59.94(2)	60.44(3)
Cu2	I2	Cu3	58.13(2)	58.512(19)	58.95(3)
Cu1	I2	Cu2	62.13(3)	62.72(2)	63.36(3)
Cu1	I2	Cu3	59.27(2)	59.70(2)	60.30(3)
Cu1	I1	Cu3	61.25(3)	61.67(2)	62.23(3)
I3	Cu2	I2	118.85(3)	118.46(3)	118.03(3)
I3	Cu2	Cu1	107.72(3)	107.36(2)	107.17(3)
I3	Cu2	Cu3	61.14(3)	60.82(2)	60.53(3)
I2	Cu2	Cu1	58.38(2)	57.96(2)	57.54(3)
Cu3	Cu2	I2	62.42(3)	62.15(2)	61.84(3)
Cu3	Cu2	Cu1	59.44(3)	59.33(2)	59.34(3)
S1	Cu2	I3	116.86(4)	116.48(3)	116.14(4)
S1	Cu2	I2	103.53(4)	103.25(3)	103.14(4)
S1	Cu2	Cu1	57.77(4)	57.46(3)	57.28(4)
S1	Cu2	Cu3	111.09(4)	110.55(3)	110.19(5)
I2	Cu1	Cu2	59.49(2)	59.32(2)	59.10(3)
I2	Cu1	Cu3	62.41(3)	62.24(2)	61.95(3)
I1	Cu1	I2	116.15(3)	116.10(3)	115.96(3)
I1	Cu1	Cu2	109.37(3)	109.05(3)	108.60(3)
I1	Cu1	Cu3	61.17(3)	61.04(2)	60.89(3)
Cu3	Cu1	Cu2	58.29(3)	58.24(2)	58.13(3)
S1	Cu1	I2	101.42(4)	101.22(3)	101.10(4)
S1	Cu1	I1	121.12(4)	120.44(3)	119.60(4)
S1	Cu1	Cu2	53.95(3)	53.51(3)	53.15(4)
S1	Cu1	Cu3	106.65(4)	106.06(3)	105.45(5)
I3	Cu3	I2	114.49(3)	114.43(3)	114.24(3)
I3	Cu3	Cu1	108.54(3)	108.54(3)	108.49(4)
I1	Cu3	I3	110.81(3)	110.56(2)	110.34(3)
I1	Cu3	I2	109.44(3)	109.14(2)	108.71(3)
I1	Cu3	Cu1	57.59(2)	57.29(2)	56.88(3)
Cu2	Cu3	I3	59.34(3)	59.23(2)	59.03(3)
Cu2	Cu3	I2	59.44(2)	59.34(2)	59.22(3)
Cu2	Cu3	I1	109.71(3)	109.42(3)	108.95(3)
Cu2	Cu3	Cu1	62.27(3)	62.42(2)	62.53(3)
Cu1	Cu3	I2	58.32(2)	58.06(2)	57.75(3)

Cu2	S1	Cu1	68.28(4)	69.03(3)	69.57(4)
P1	S1	Cu2	100.17(6)	100.39(5)	100.54(6)
P1	S1	Cu1	115.43(7)	116.32(5)	117.11(6)
Symmetry codes: [1]1/2+X,+Y,1/2-Z; [2]3/2-X,-1/2+Y,+Z; [3]+X,1/2-Y,-1/2+Z; [4]3/2-X,1/2+Y,+Z; [5]-1/2+X,+Y,1/2-Z; [6]+X,1/2-Y,1/2+Z.					

Table S7. Bond angles of **2** at 100 K, 200 K, 298 K.

Atom1	Atom2	Atom3	Angle-100 K(˚)	Angle-200 K(˚)	Angle-298 K(˚)
Cu2	I3	Cu3	60.445(15)	60.76(2)	61.01(2)
Cu1	I2	Cu2	62.722(15)	63.39(2)	64.27(2)
Cu1	I2	Cu3	57.201(14)	57.60(2)	58.14(2)
Cu2	I2	Cu3	58.295(14)	58.55(2)	58.77(2)
Cu1	I1	Cu3	59.042(15)	59.47(2)	60.01(2)
I2	Cu1	Cu2	59.505(14)	59.24(2)	58.82(2)
I1	Cu1	I2	120.848(19)	120.66(3)	120.33(3)
I1	Cu1	Cu2	109.661(19)	109.35(3)	108.99(3)
I1	Cu1	Cu3	62.514(16)	62.39(2)	62.31(2)
Cu3	Cu1	I2	64.225(16)	64.04(2)	63.70(2)
Cu3	Cu1	Cu2	59.426(17)	59.19(3)	58.71(3)
S1	Cu1	I2	101.37(2)	100.85(4)	100.01(3)
S1	Cu1	I1	115.28(2)	115.13(4)	115.38(4)
S1	Cu1	Cu2	52.49(2)	52.05(3)	51.61(3)
S1	Cu1	Cu3	104.87(3)	104.21(4)	103.52(4)
I3	Cu2	I2	116.455(18)	116.40(3)	116.56(3)
I3	Cu2	Cu1	108.350(18)	107.94(3)	107.46(3)
I3	Cu2	Cu3	60.719(15)	60.49(2)	60.33(2)
I2	Cu2	Cu1	57.772(14)	57.37(2)	56.91(2)
Cu3	Cu2	I2	62.670(15)	62.48(2)	62.29(2)
Cu3	Cu2	Cu1	57.055(17)	56.98(2)	56.94(2)
S1	Cu2	I3	117.97(2)	117.58(4)	117.25(4)
S1	Cu2	I2	104.03(2)	103.68(3)	102.97(4)
S1	Cu2	Cu1	57.55(2)	57.43(3)	57.19(3)
S1	Cu2	Cu3	107.18(3)	106.95(4)	106.83(4)
I3	Cu3	I2	111.605(17)	111.75(3)	112.07(3)
I3	Cu3	I1	113.005(17)	112.83(3)	112.57(3)
I1	Cu3	I2	112.118(17)	111.73(2)	111.15(3)
Cu1	Cu3	I3	112.15(2)	112.17(3)	112.16(3)
Cu1	Cu3	I2	58.574(15)	58.37(2)	58.16(2)
Cu1	Cu3	I1	58.443(15)	58.14(2)	57.67(2)
Cu1	Cu3	Cu2	63.519(18)	63.84(3)	64.34(3)
Cu2	Cu3	I3	58.835(14)	58.75(2)	58.65(2)

Cu2	Cu3	I2	59.035(14)	58.97(2)	58.94(2)
Cu2	Cu3	I1	109.697(19)	109.70(3)	109.81(3)
Cu2	S1	Cu1	69.95(2)	70.52(3)	71.20(4)
P1	S1	Cu1	119.49(4)	119.69(6)	119.59(6)
P1	S1	Cu2	101.54(4)	101.81(5)	102.13(5)
Symmetry codes: [1]1/2-X,1/2+Y,+Z; [2]-1/2+X,+Y,1/2-Z; [3]+X,3/2-Y,-1/2+Z; [4]1/2-X,-1/2+Y,+Z; [5]1/2+X,+Y,1/2-Z; [6]+X,3/2-Y,1/2+Z.					