Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Quasi-Linear CuX_2 (X = Cl, Br) Motif-Built Hybrid Copper Halides Realizing Encouraging Nonlinear Optical Activities

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Contents

Table S1. Crystal data and structure refinement of $(C_{20}H_{20}P)CuX_2$ (X=Cl, Br).

Empirical formula	$C_{20}H_{20}PCuCl_2$	$C_{20}H_{20}PCuBr_2$
Formula weight	425.77	514.69
Temperature/(K)	296	296
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
a/Å	9.4777(4)	9.7557(4)
b/Å	12.2690(6)	12.2416(5)
c/Å	9.6477(4)	9.7625(4)
α/°	90	90
β/°	117.7870(10)	118.6090(10)
γ/°	90	90
Volume/Å^3	992.49(8)	1023.54(7)
Z	2	2
ρ_{calc} g/cm^3	1.425	1.67
μ/mm^{-1}	1.449	5.048
F(000)	436	508
2θ range for data collection/°	4.772 to 56.724	4.752 to 59.372
Index ranges	$-12 \le h \le 10$, $-16 \le k \le 16$, $-10 \le l \le 12$	$-13 \le h \le 13$, $-16 \le k \le 17$, $-13 \le l \le 13$
Reflections collected	14950	16823
Independent reflections	4928 [R_{int} = 0.0299, R_{sigma} = 0.0486]	5718 [R_{int} = 0.0598, R_{sigma} = 0.0579]
Data/restraints/parameters	4928/1/218	5718/1/218
Goodness-of-fit on F^2	1.032	1.019
Final R indexes [I>=2σ (I)]	R1 = 0.0366, wR2 = 0.0663	R1 = 0.0419, wR2 = 0.0758
Final R indexes [all data]	R1 = 0.0641, wR2 = 0.0740	R1 = 0.0846, wR2 = 0.0865
Largest diff. peak/hole/e Å^{-3}	0.20/-0.21	0.36/-0.30
Flack parameter	0.015(6)	-0.013(6)

$R1 = \Sigma||F_o|-|F_c|| / \Sigma|Fo|$, $wR2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2)+(0.0462P)^2]$ where $P = (F_o^2+2F_c^2)/3$

Table S2. Fractional atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $(C_{20}H_{20}P)CuX_2$ (X = Cl, Br).

Atom	*x*	*y*	*x*	U_{eq}[a]
		$(C_{20}H_{20}P)CuCl_2$		
Cu (1)	1133.2(5)	5460.3(4)	975.8(5)	65.69(18)
Cl (1)	908.2(12)	6033.0(11)	2905.0(13)	74.9(3)
Cl (2)	1308.5(14)	4977.0(13)	-1010.5(14)	96.8(5)
P (1)	5793.8(9)	4308.6(7)	6654.4(9)	37.07(19)
C (1)	7202(5)	3188(4)	9525(4)	69.1(12)
C (2)	7375(4)	3483(3)	8076(4)	49.7(9)
C (3)	3930(4)	3602(3)	5924(4)	41.5(8)
C (4)	3110(4)	3585(3)	6799(4)	48.3(9)
C (5)	1727(4)	2992(3)	6290(5)	56.9(10)
C (6)	1136(4)	2427(4)	4894(5)	61.3(11)
C (7)	1928(5)	2448(3)	4014(5)	59.4(10)
C (8)	3332(4)	3029(3)	4526(4)	50.3(9)
C (9)	6245(4)	4621(3)	5086(3)	36.9(7)
C (10)	5129(4)	5194(3)	3800(4)	48.3(9)
C (11)	5478(4)	5480(4)	2615(4)	56.6(9)
C (12)	6946(4)	5233(3)	2729(4)	54.8(10)
C (13)	8055(4)	4684(3)	3999(4)	55.1(9)
C (14)	7709(4)	4367(3)	5181(4)	47.3(8)
C (15)	5662(4)	5561(3)	7546(3)	39.3(7)
C (16)	7036(4)	6027(3)	8695(4)	49.2(9)
C (17)	6992(6)	7028(3)	9319(4)	61.6(11)
C (18)	5582(5)	7571(3)	8804(4)	59.2(10)
C (19)	4205(5)	7119(3)	7669(5)	62.9(11)
C (20)	4233(4)	6118(3)	7030(4)	51.4(9)
		$(C_{20}H_{20}P)CuBr_2$		
Cu (1)	9044.2(9)	4525.9(6)	8869.7(8)	63.3(2)
Br (1)	7029.4(7)	3993.0(6)	9163.4(7)	71.4(2)
Br (2)	11140.6(8)	4945.6(6)	8660.9(8)	82.3(2)
P (1)	3311.5(14)	5701.5(9)	4198.6(13)	36.2(3)
C (1)	6145(6)	4801(4)	4851(5)	48.9(12)
C (2)	7311(6)	4500(5)	4524(7)	56.8(14)
C (3)	7218(7)	4789(5)	3110(7)	56.0(14)
C (4)	5971(7)	5373(5)	2048(6)	55.5(14)

Atom	*x*	*y*	*x*	U_{eq}[a]
C (5)	4779(6)	5683(4)	2362(6)	48.7(12)
C (6)	4869(6)	5394(4)	3771(5)	37.9(10)
C (7)	2943(6)	3913(4)	5740(6)	48.7(12)
C (8)	2308(7)	2904(5)	5757(7)	60.3(15)
C (9)	1185(7)	2452(5)	4424(8)	61.0(15)
C (10)	668(7)	2966(5)	3023(8)	58.9(14)
C (11)	1281(6)	3966(5)	2978(6)	50.0(12)
C (12)	2438(5)	4447(4)	4335(5)	38.6(10)
C (13)	3233(6)	6444(4)	6839(6)	48.4(12)
C (14)	3778(7)	7018(5)	8197(7)	56.9(14)
C (15)	5179(7)	7571(5)	8781(6)	60.0(15)
C (16)	6023(7)	7544(5)	7988(7)	59.0(15)
C (17)	5473(6)	6969(4)	6602(6)	49.2(13)
C (18)	4083(6)	6410(4)	6023(5)	40.0(11)
C (19)	1880(6)	6527(4)	2651(6)	51.4(13)
C (20)	447(7)	6776(5)	2820(9)	69.6(18)

[a]U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Table S3. Bond lengths for $(C_{20}H_{20}P)CuX_2$ (X = Cl, Br)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
		$(C_{20}H_{20}P)CuCl_2$			
Cu (1)	Cl (1)	2.091(1)	C (10)	C 11)	1.376(4)
Cu (1)	Cl (2)	2.085(1)	C (10)	C (9)	1.388(4)
P (1)	C (15)	1.794(4)	C (12)	C (11)	1.377(5)
P (1)	C (3)	1.791(3)	C (12)	C (13)	1.364(5)
P (1)	C (2)	1.800(3)	C (14)	C (13)	1.382(5)
P (1)	C (9)	1.795(3)	C (14)	C (9)	1.383(4)
C (2)	C (1)	1.525(5)	C (15)	C (20)	1.386(4)
C (3)	C (8)	1.386(5)	C (15)	C (16)	1.380(5)
C (3)	C (4)	1.389(4)	C (17)	C (16)	1.377(5)
C (4)	C (5)	1.373(5)	C (17)	C (18)	1.362(6)
C (6)	C (7)	1.370(5)	C (18)	C (19)	1.371(6)
C (6)	C (5)	1.380(5)	C (20)	C (19)	1.379(5)
C (7)	C (8)	1.382(5)			
		$(C_{20}H_{20}P)CuBr_2$			
Cu (1)	Br (1)	2.216(1)	C (9)	C (8)	1.355(8)
Cu (1)	Br (2)	2.211(9)	C (10)	C (9)	1.364(9)
P (1)	C (6)	1.798(5)	C (11)	C (10)	1.372(8)
P (1)	C (12)	1.792(5)	C (12)	C (11)	1.394(7)
P (1)	C (18)	1.790(5)	C (12)	C (7)	1.380(6)
P (1)	C (19)	1.798(5)	C (13)	C (14)	1.363(7)
C (2)	C (1)	1.371(7)	C (15)	C (16)	1.375(8)
C (2)	C (3)	1.386(8	C (15)	C (14)	1.380(8)
C (3)	C (4)	1.363(8)	C (16)	C (17)	1.385(7)
C (5)	C (4)	1.390(7)	C (18)	C (13)	1.399(7)
C (6)	C (1)	1.390(7)	C (18)	C (17)	1.376(7)
C (6)	C (5)	1.381(6)	C (19)	C (20)	1.515(8)
C (7)	C (8)	1.386(8)			

Table S4. Bond angles for $(C_{20}H_{20}P)CuX_2$ (X = Cl, Br).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
			$(C_{20}H_{20}P)CuCl_2$				
Cl (2)	Cu (1)	Cl (1)	176.66(6)	C (10)	C (11)	C (12)	120.2(3)
C (15)	P (1)	C (2)	109.66(15)	C (10)	C (9)	P (1)	118.7(2)
C (15)	P (1)	C (9)	108.58(15)	C (11)	C (10)	C (9)	119.6(3)
C (3)	P (1)	C (15)	109.08(15)	C (12)	C (13)	C (14)	120.0(3)
C (3)	P (1)	C (2)	110.21(17)	C (13)	C (14)	C (9)	119.9(3)
C (3)	P (1)	C (9)	110.52(14)	C (13)	C (12)	C (11)	120.5(3)
C (9)	P (1)	C (2)	108.76(15)	C (14)	C (9)	P (1)	121.4(3)
C (1)	C (2)	P (1)	115.1(2)	C (14)	C (9)	C (10)	119.8(3)
C (4)	C (3)	P (1)	119.8(3)	C (16)	C (15)	P (1)	119.3(3)
C (4)	C (5)	C (6)	120.1(3)	C (16)	C (15)	C (20)	118.9(3)
C (5)	C (4)	C (3)	120.1(3)	C (17)	C (16)	C (15)	120.7(4)
C (6)	C (7)	C (8)	120.2(4)	C (17)	C (18)	C (19)	120.0(4)
C (7)	C (6)	C (5)	120.3(4)	C (18)	C (17)	C (16)	120.1(4)
C (7)	C (8)	C (3)	119.9(3)	C (18)	C (19)	C (20)	120.5(4)
C (8)	C (3)	P (1)	120.6(2)	C (19)	C (20)	C (15)	119.8(4)
C (8)	C (3)	C (4)	119.5(3)	C (20)	C (15)	P (1)	121.7(3)
			$(C_{20}H_{20}P)CuBr_2$				
Br (2)	Cu (1)	Br (1)	175.8(5)	C (11)	C (12)	P (1)	119.3(4)
C (1)	C (2)	C (3)	119.8(5)	C (12)	P (1)	C (6)	108.8(2)
C (1)	C (6)	P (1)	118.9(3)	C (12)	P (1)	C (19)	109.8(2)
C (2)	C (1)	C (6)	120.4(4)	C (12)	C (7)	C (8)	119.0(5)
C (3)	C (4)	C (5)	120.8(5)	C (13)	C (18)	P (1)	120.0(4)
C (4)	C (3)	C (2)	120.0(5)	C (13)	C (14)	C (15)	120.2(5)
C (5)	C (6)	P (1)	121.3(4)	C (14)	C (13)	C (18)	120.5(5)
C (5)	C (6)	C (1)	119.7(4)	C (15)	C (16)	C (17)	120.4(6)
C (6)	C (5)	C (4)	119.2(5)	C (16)	C (15)	C (14)	119.8(5)
C (6)	P (1)	C (19)	109.0(2)	C (17)	C (18)	P (1)	120.8(4)
C (7)	C (12)	P (1)	121.6(4)	C (17)	C (18)	C (13)	119.2(5)
C (7)	C (12)	C (11)	119.1(4)	C (18)	P (1)	C (12)	109.2(2)
C (8)	C (9)	C (10)	121.0(5)	C (18)	P (1)	C (6)	109.5(2)
C (9)	C (10)	C (11)	119.1(5)	C (18)	P (1)	C (19)	110.6(2)
C (9)	C (8)	C (7)	120.9(5)	C (18)	C (17)	C (16)	119.9(5)
C (10)	C (11)	C (12)	120.9(5)	C (20)	C (19)	P (1)	114.1(4)

Table S5. The *x*/*y*/*z*-projections of local dipole moment (DM) of $[CuX]^-$ in one-unit cell of $(C_{20}H_{20}P)CuX_2$ (X = Cl, Br).

Ion	μ_x (D)	μ_y (D)	μ_z (D)
		$C_{20}H_{20}PCuCl_2$	
$[CuCl_2]^-$	0.197	-0.142	-0.288
$[CuCl_2]^-$	-0.197	-0.142	0.288
Total $[CuCl_2]^-$	0	-0.284	0
		$C_{20}H_{20}PCuBr_2$	
$[CuBr_2]^-$	-1.225	0.757	1.597
$[CuBr_2]^-$	1.225	0.757	-1.597
Total $[CuBr_2]^-$	0	1.514	0

Table S6. Point charge model analysis of $(C_{20}H_{20}P)CuX_2$ (X=Cl, Br). According to the crystal structure data collected at 296 K, we select a unit cell and assume that the centers of the positive charges of the organic cations and the negative charges of the $(CuX_2)^{2-}$ are located on the P atoms and Cu atoms, respectively.

<table>
<tr><td colspan="3">$(C_{20}H_{20}P)CuCl_2$</td></tr>
<tr><td>Atom</td><td>Atom coordinate</td><td>Coordinate of charge center</td></tr>
<tr><td>Cu1</td><td>(0.8867,0.0462,0.9024)</td><td rowspan="2">（0.5,0.2960,0.5）</td></tr>
<tr><td>Cu1'</td><td>(0.1133,0.5460,0.0976)</td></tr>
<tr><td>P1</td><td>(0.5794,0.4309,0.6654)</td><td rowspan="2">(0.5,0.6808,0.5)</td></tr>
<tr><td>P1'</td><td>(0.4206,0.9308,0.3346)</td></tr>
<tr><td colspan="3">μ_{total} = (0.6808-0.2960) × b × 2e = 0.3848 × 12.2690 × 10^{-10} m × 2 ×1.6×10^{-19} C
= 1.5626×10^{-28} C·m = 48.678 D</td></tr>
<tr><td colspan="3">$(C_{20}H_{20}P)CuBr_2$</td></tr>
<tr><td>Atom</td><td>Atom coordinate</td><td>Coordinate of charge center</td></tr>
<tr><td>Cu1</td><td>（0.1129,0.9552,0.0956）</td><td rowspan="2">（0.5,0.7026,0.5）</td></tr>
<tr><td>Cu1'</td><td>(0.8871,0.4550,0.9044)</td></tr>
<tr><td>P1</td><td>(0.5804,0.0722,0.6689)</td><td rowspan="2">(0.5,0.3201,0.5)</td></tr>
<tr><td>P1'</td><td>(0.4196,0.5722,0.3311)</td></tr>
<tr><td colspan="3">μ_{total} = (0.3201-0.7026) × b × 2e = -0.3825 × 12.2319 × 10^{-10} m × 2 ×1.6×10^{-19} C
= -1.4971×10^{-28} C·m = 46.638 D</td></tr>
</table>

Table S7. Bond valence sum of Cu^{+} ion in $(C_{20}H_{20}P)CuX_2$ (X = Cl, Br).

Compound	Bond	Bond distance/Å	Bond valence	Sum
$(C_{20}H_{20}P)CuCl_2$	Cu-Cl(1)	2.0914	0.580233701	1.17027216
	Cu-Cl(2)	2.0852	0.590038454	
$(C_{20}H_{20}P)CuBr_2$	Cu-Br(1)	2.2143	0.607679236	1.22030563
	Cu-Br(2)	2.2113	0.612626394	

Table S8. Comparison of structural feature and optical performance for $ACuX_2$ (A= organic cation, X = Cl, Br)

Compound	Structure	SHG	PL / nm	Band gap Type	Optical Band gap /eV	Theoretical Band gap /eV	Ref.
$(C_{12}H_{20}N)CuCl_2$	CS	-	505	Direct	4.05	3.82	1
$(C_{12}H_{20}N)CuBr_2$	CS	-	507	Direct	3.13	-	2
$(C_{16}H_{28}N)CuCl_2$	CS	-	510	Direct	3.43	3.85	3
$(C_{16}H_{28}N)CuBr_2$	CS	-	498	Direct	3.92	3.38	4
$(C_{24}H_{20}P)CuCl_2$	NCS	No report	562	-	3.67	-	5
$(C_{24}H_{20}P)CuBr_2$	CS	-	526	-	3.67	-	5
$(C_{24}H_{20}P)CuBr_2$	CS	-	526	-	2.57	2.09	6
$(C_{20}H_{20}P)CuCl_2$	NCS	1.1 × KDP	523	Indirect	3.56	2.43	this work
$(C_{20}H_{20}P)CuBr_2$	NCS	0.89 × KDP	533	Indirect	3.64	2.52	this work

Note: CS-centrosymmetric; NCS-noncentrosymmetric

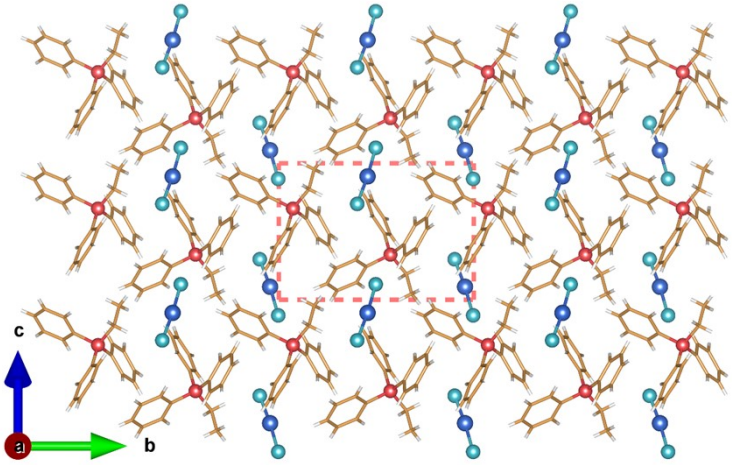

Figure S1. Crystal structure of $(C_{20}H_{20}P)CuBr_2$.

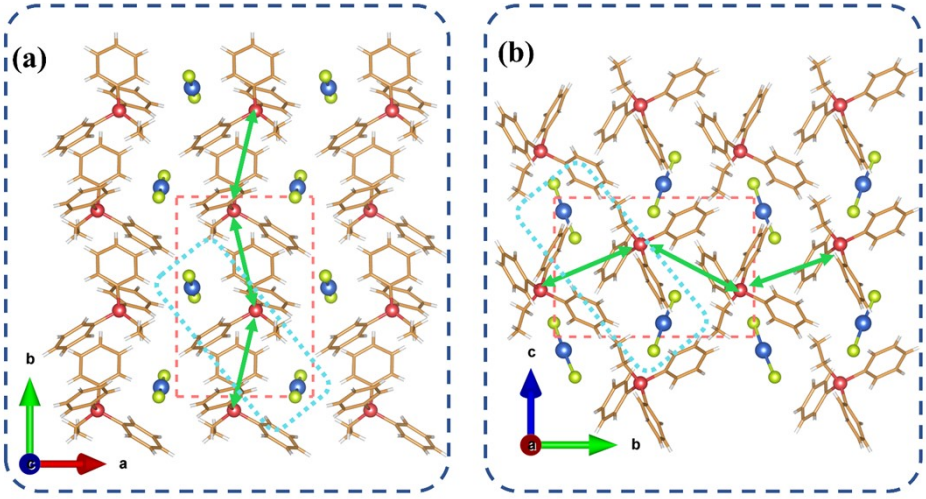

Figure S2 Structure of $(C_{20}H_{20}P)CuCl_2$ viewed along the *c*-axis (a) and *a*-axis (b)

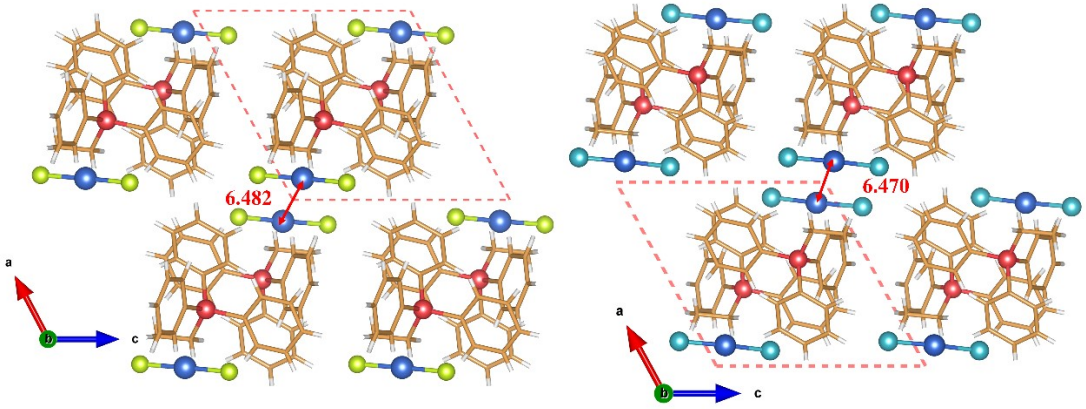

Figure S3. The nearest distance of Cu···Cu in $(C_{20}H_{20}P)CuCl_2$ (a) and $(C_{20}H_{20}P)CuBr_2$ (b).

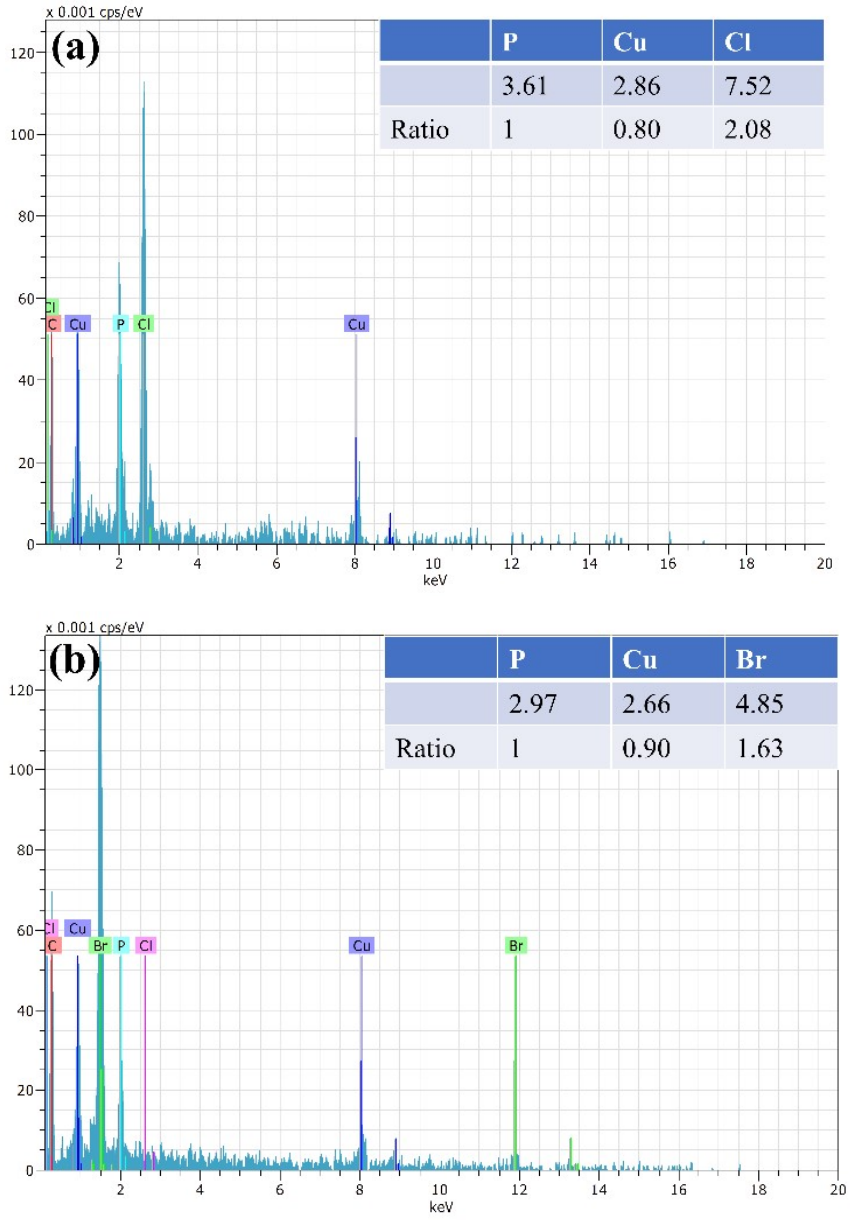

Figure S4. The EDS analysis for $(C_{20}H_{20}P)CuCl_2$ (a) and $(C_{20}H_{20}P)CuBr_2$ (b).

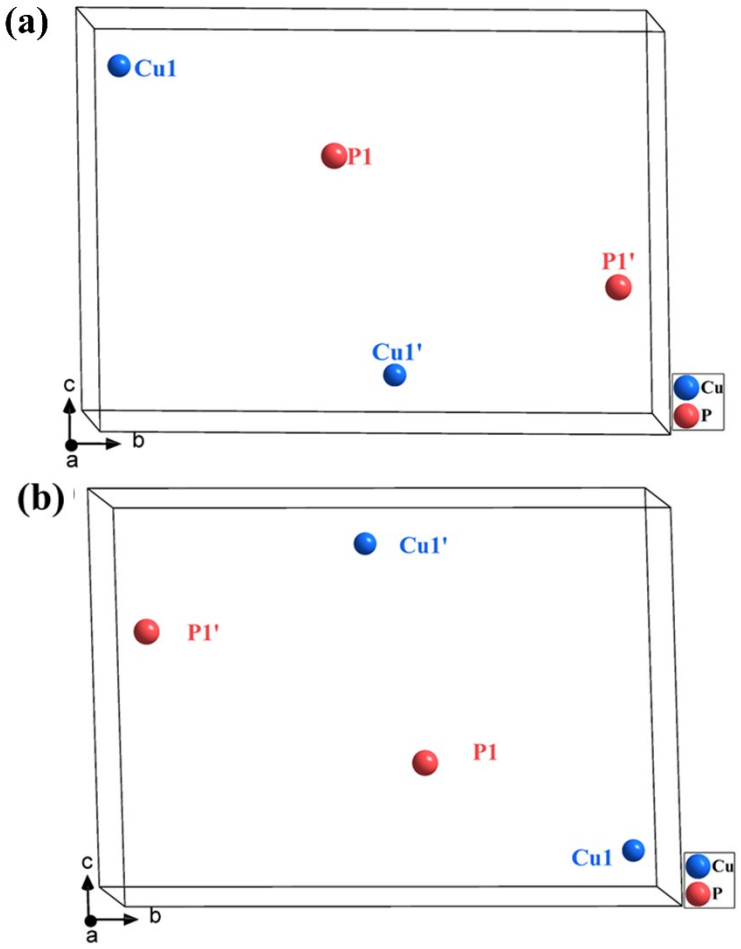

Figure S5. Distribution of P and Cu atoms in unit cells of $(C_{20}H_{20}P)CuCl_2$ (a) and $(C_{20}H_{20}P)CuBr_2$ (b).

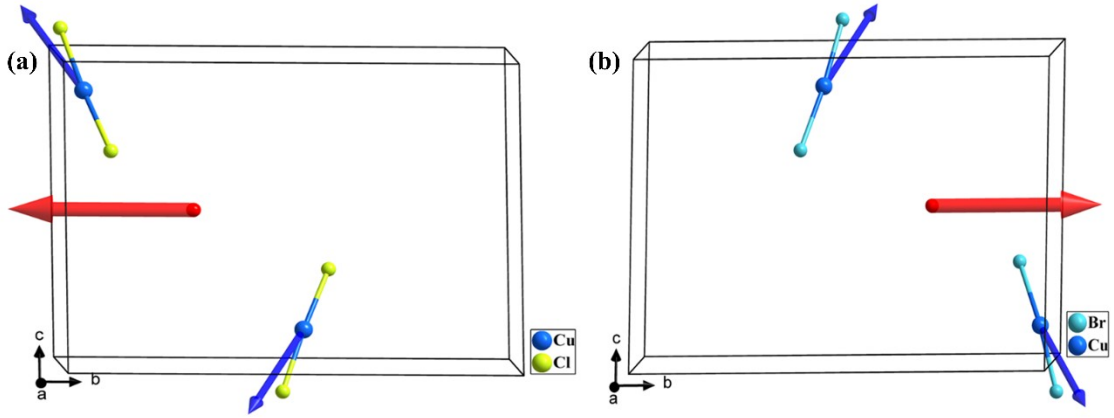

Figure S6. Dipole moments of $[CuX_2]^-$ in one-unit cell. (a) $(C_{20}H_{20}P)CuCl_2$; (b) $(C_{20}H_{20}P)CuBr_2$; Blue: $[CuX_2]^-$. The red arrows in the middle present the total dipole moments of the inorganic parts.

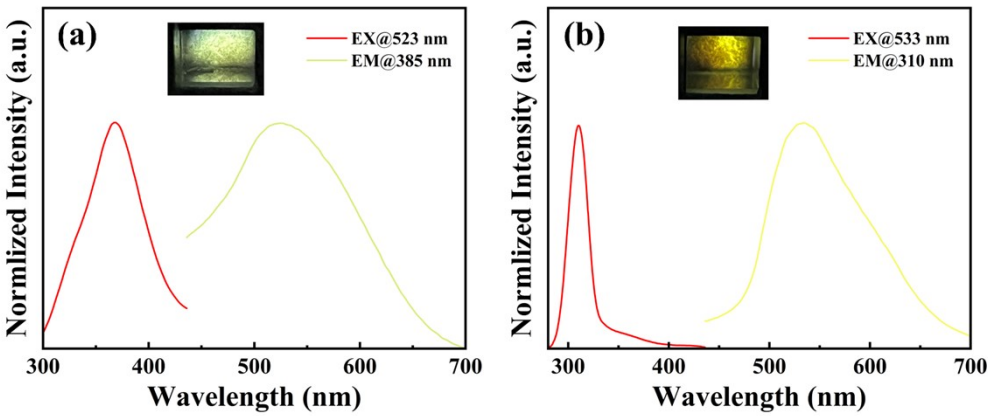

Figure S7. PLE and PL spectra of $(C_{20}H_{20}P)CuCl_2$ (a) and $(C_{20}H_{20}P)CuBr_2$ (b).

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