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Structural characterization and luminescence properties of trigonal Cu(I) iodine/bromine complexes comprising cation–π interactions†

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Table S1 Crystal parameters of complexes **1**, **2** and **3.**

Compound reference	**1**	**2**	**3**
Formula	$C_{43}H_{32}CuIN_2P_2$	$C_{43}H_{32}CuBrN_2P_2$	$C_{43}H_{32}CuClN_2P_2$
Temperature/K	291.15	291(2)	293(2)
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$
a/Å	10.656(2)	10.6373(18)	18.975(4)
b/Å	17.374(3)	17.157(3)	11.948(2)
c/Å	20.131(4)	19.959(3)	17.490(3)
α/°	90	90	90
β/°	90	90	113.44(3)
γ/°	90	90	90
Volume/Å^3	3727.2(12)	3642.7(11)	3638.0(12)
Z	4	4	4
$\rho_{calc.}$ / g·cm^3	1.478	1.426	1.403
μ / mm^{-1}	1.533	1.818	0.799
F (000)	1665.4	1582.0	1586.0
Radiation	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.32 to 55.06	6.08 to 54.964°	4.25 to 52.744
Reflections collected	64211	51998	55089
Independent reflections	8546 [R(int) = 0.0368, R_{sigma} = 0.0257]	8321[R(int) = 0.0477, R_{sigma} = 0.0442]	7417 [R(int) = 0.0724, R_{sigma} = 0.0471]
Data/restraints/parameters	8546/0/443	8321/0/442	7417/937/884
Goodness-of-fit on F^2	1.055	1.022	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0234 wR_2 = 0.0467	R_1 = 0.0305 wR_2 = 0.0600	R_1 = 0.0436 wR_2=0.1070
CCDC	2129756	2129758	2129759

Table S2 Selected bond lengths [Å] and angles (°) for the Cu(I) complexes **1**, **2** and **3**.

Complex	Length/Å		Angle/°	
1	Cu1-P1	2.2808(7)	I1-Cu1-P1	119.612(17)
	Cu1-P2	2.2514(7)	I1-Cu1-P2	116.265(18)
	Cu1-I1	2.5258(4)	P1-Cu1-P2	121.31(2)
2	Cu1-P1	2.2706(10)	Br1-Cu1-P1	119.24(3)
	Cu1-P2	2.2432(9)	Br1-Cu1-P2	117.28(3)
	Cu1-Br1	2.3410(6)	P1-Cu1-P2	120.76(4)
3	Cu1-P1	2.241(4)	Cl1-Cu1-P1	119.5(2)
	Cu1-P2	2.251(5)	Cl1-Cu1-P2	113.7(2)
	Cu1-Cl1	2.200(6)	P1-Cu1-P2	125.3(2)

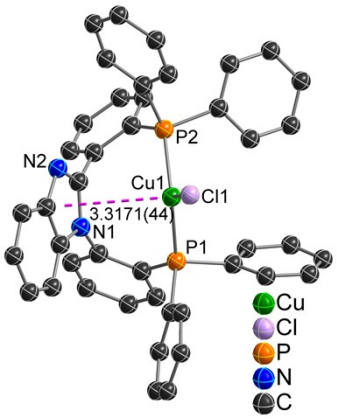

Fig. S1 Molecular structure of the Cu(I) complex **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoid plots at 30% probability.

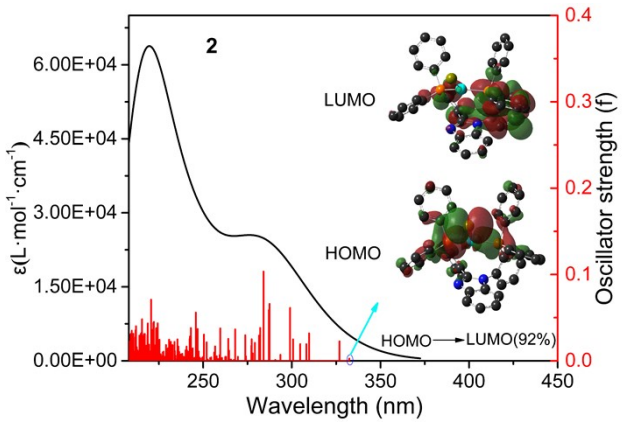

Fig. S2 Simulated absorption spectrum of **2** with frontier molecular orbitals involved in the lowest energy transition.

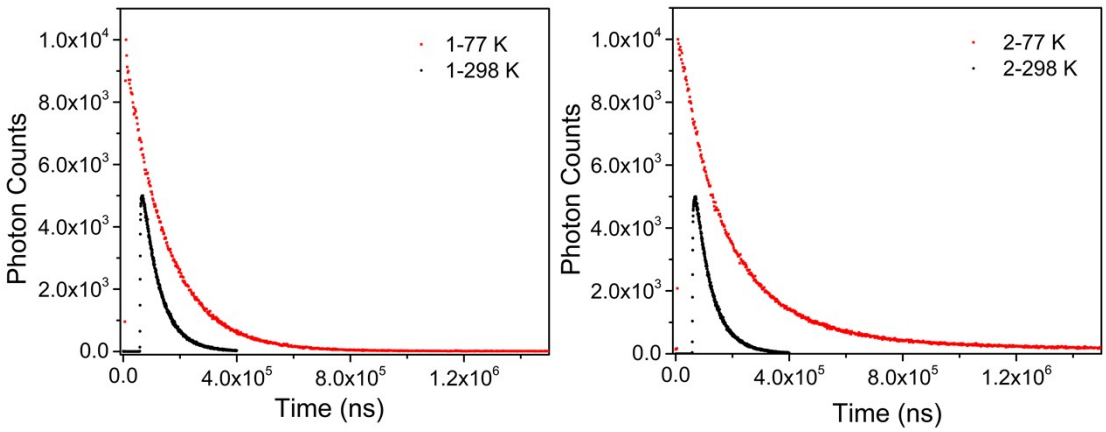

Fig. S3 Emission decay transient of copper(I) complexes **1** and **2** at different temperature (black dot for 298 K, red dot for 77 K).

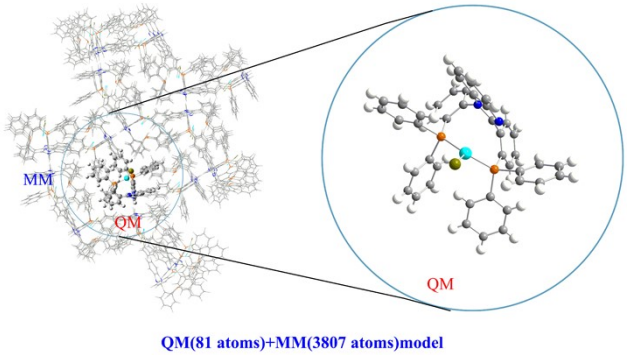

Fig. S4 ONIOM model for complex **2**: the central molecule is defined as the active QM part and the surrounding molecules are treated as MM part.