Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Doping effect on a two-electron silver nanocluster

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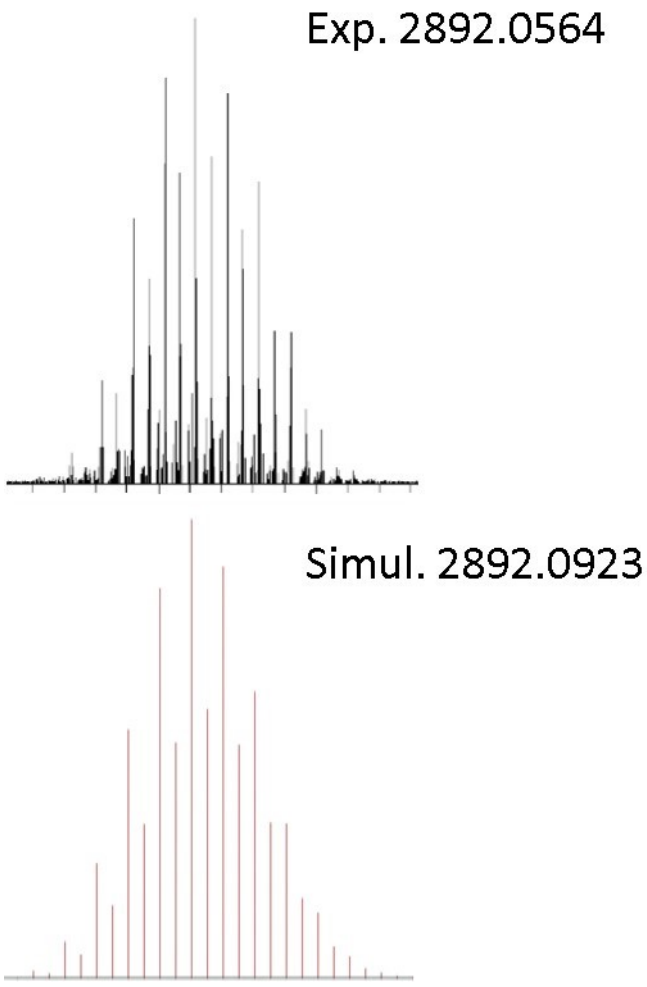


Fig. S1 The experimental (top) and simulated isotope distribution pattern of $[Ag_{11}\{S_{2P}(O^iPr)_2\}_8]$ in the ESI-MS of $\mathbf{Cu_xAg_{11-x}}$.

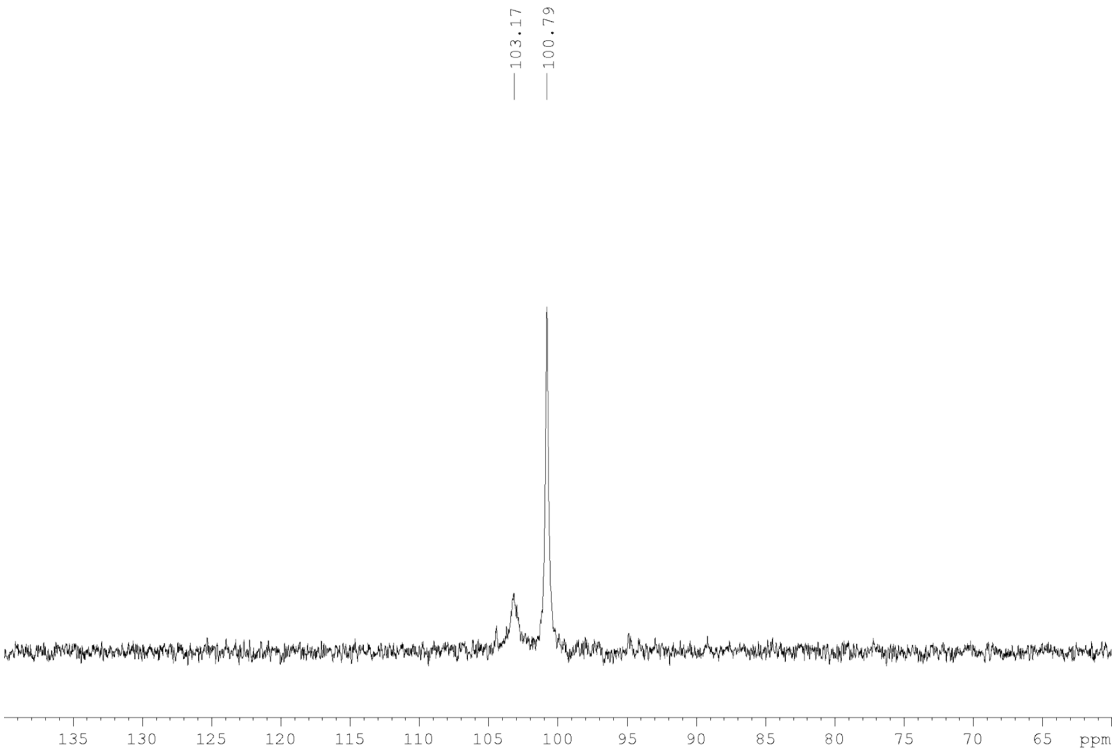


Fig. S2 The $^{31}P\{^{1}H\}$ NMR spectrum of **Ag_{11}** (in $CDCl_3$).

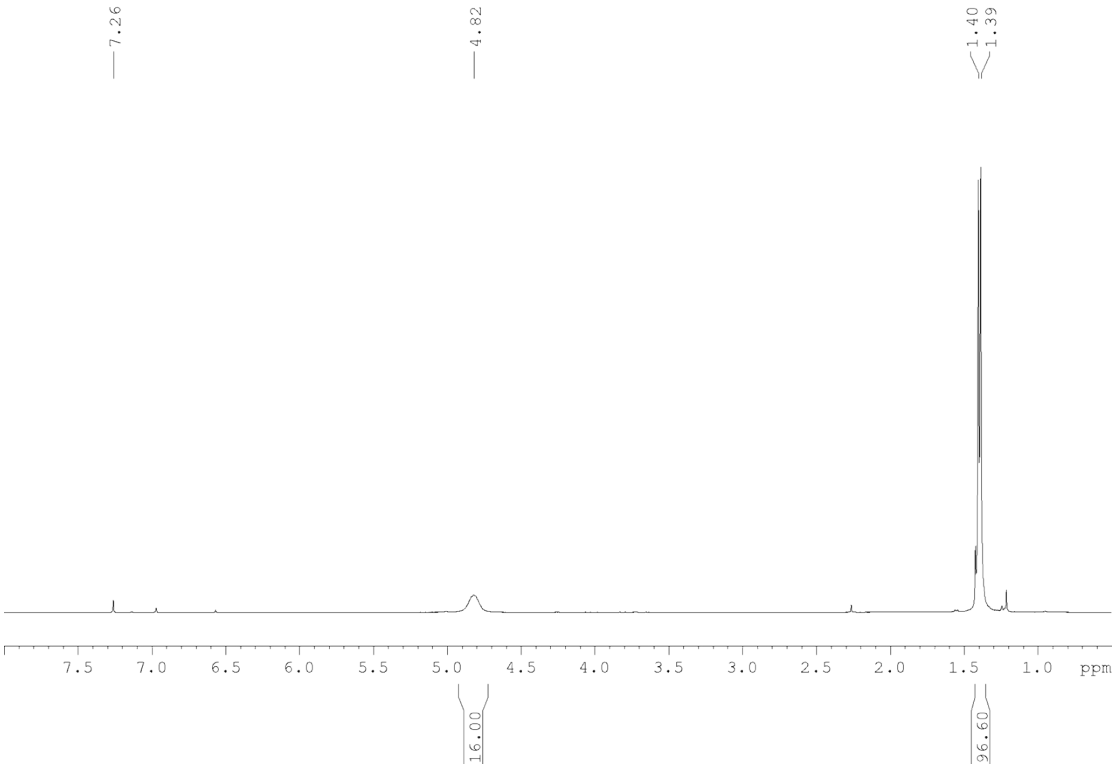


Fig. S3 The ^{1}H NMR spectrum of **Ag_{11}** (in $CDCl_3$).

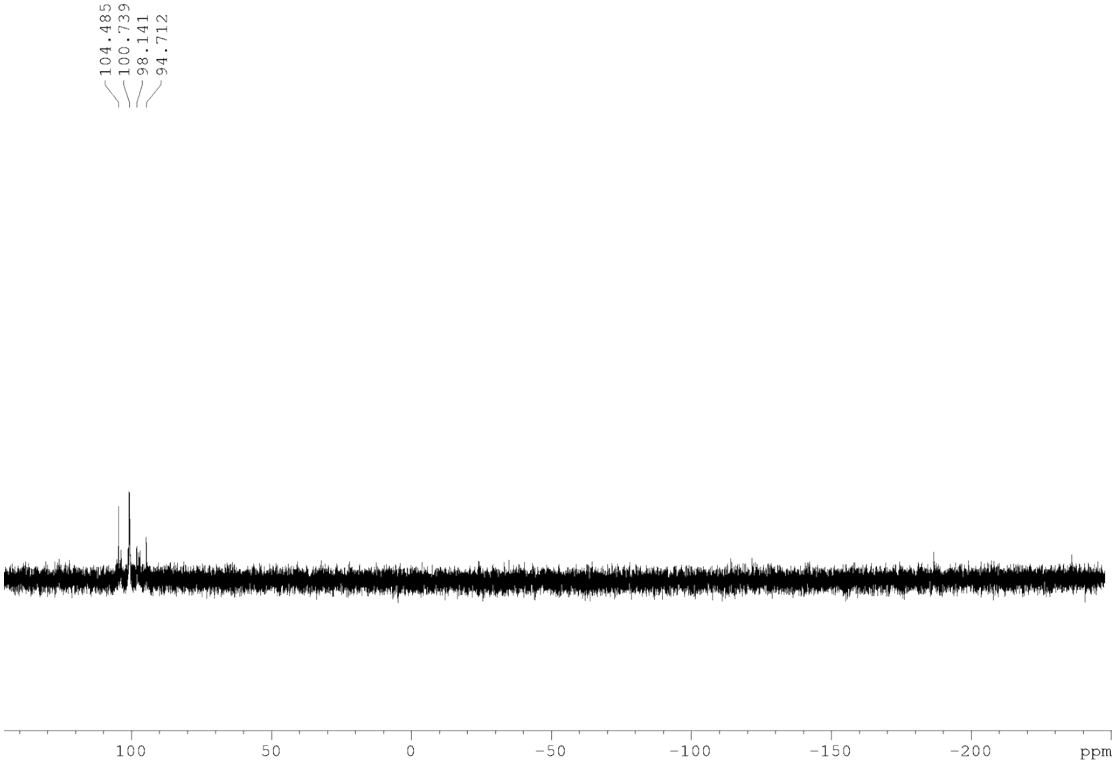


Fig. S4 The $^{31}P\{^{1}H\}$ NMR spectrum of $\mathbf{Cu_xAg_{11-x}}$ (in $CDCl_3$).

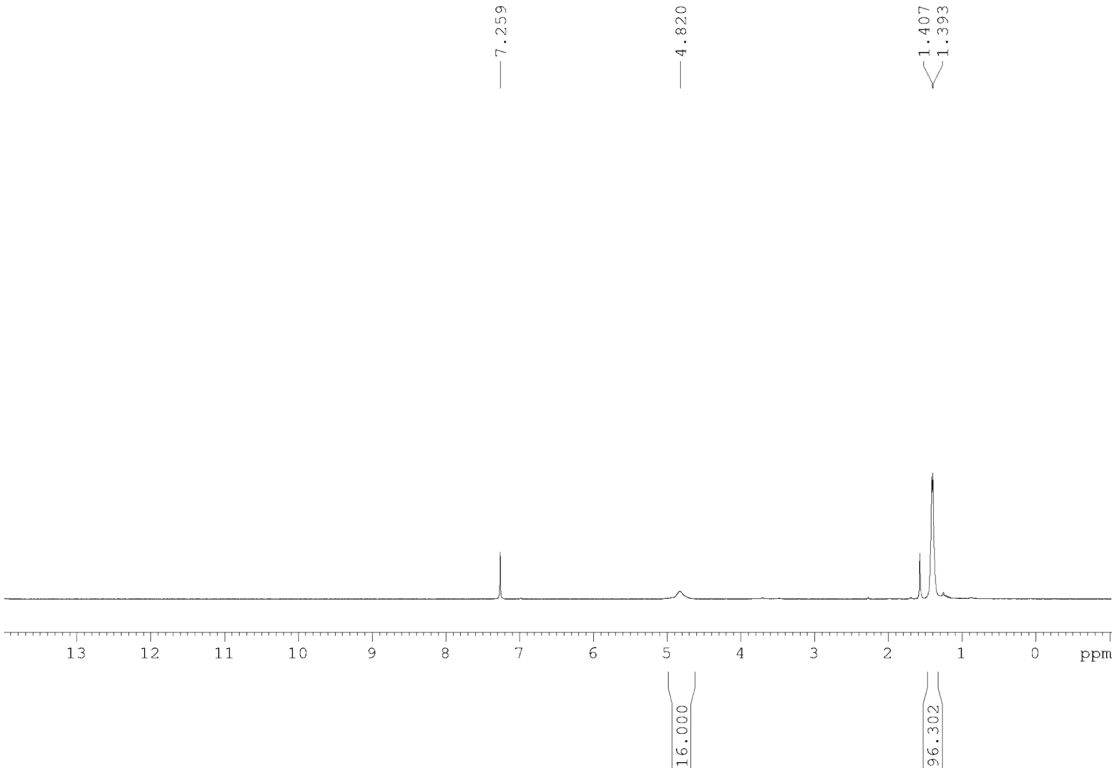


Fig. S5 The ^{1}H NMR spectrum of $\mathbf{Cu_xAg_{11-x}}$ (in $CDCl_3$).

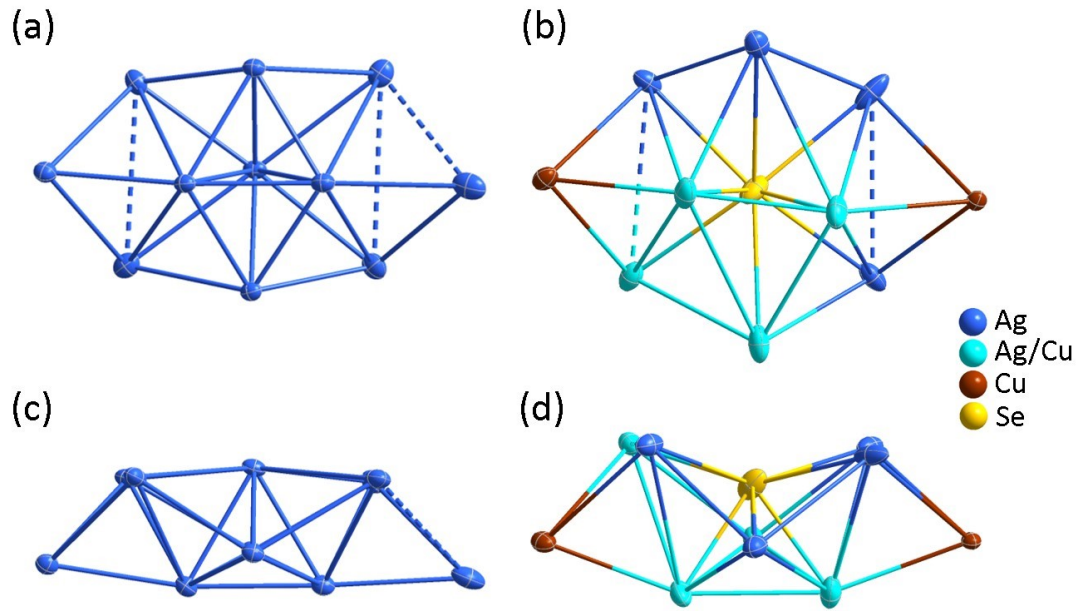


Fig. S6 (a) The metal framework in **Ag_{11}** and (b) $[Cu_xAg_{10-x}(Se)\{Se_2P(O^iPr)_2\}_8]$. (c)A side view of the metal framework in **Ag_{11}** and (d) $[Cu_xAg_{10-x}(Se)\{Se_2P(O^iPr)_2\}_8]$.

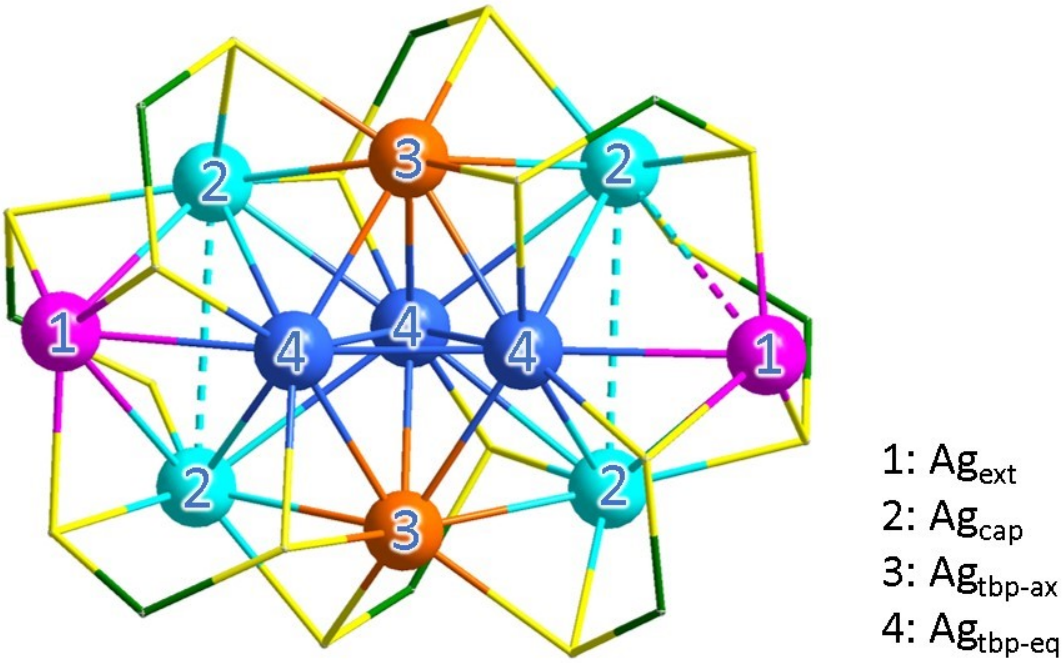


Fig. S7 A schematic diagram of the replacement of Cu atoms in **Cu_xAg_{11-x}**.

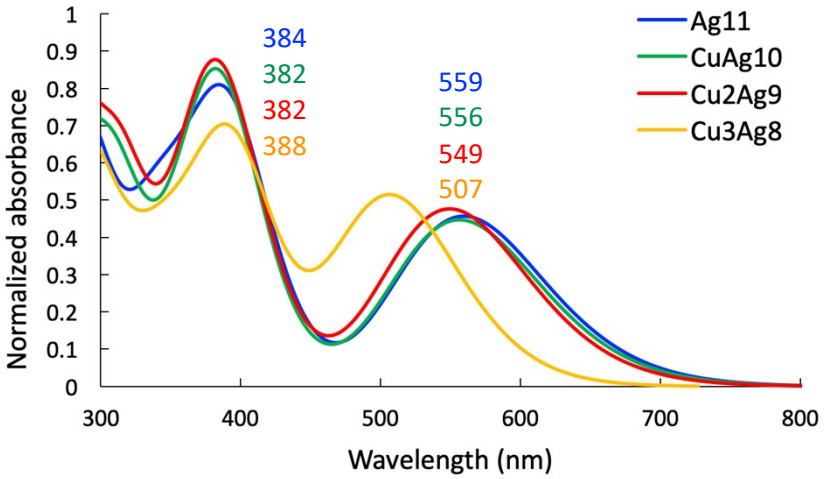


Fig. S8 The TD-DFT-simulated spectra of $\mathbf{Ag_{11}}$ and the $\mathbf{Cu_xAg_{(11-x)}}$ (x = 1-3) alloys considered in their configuration of lowest energy (see Figure 4).

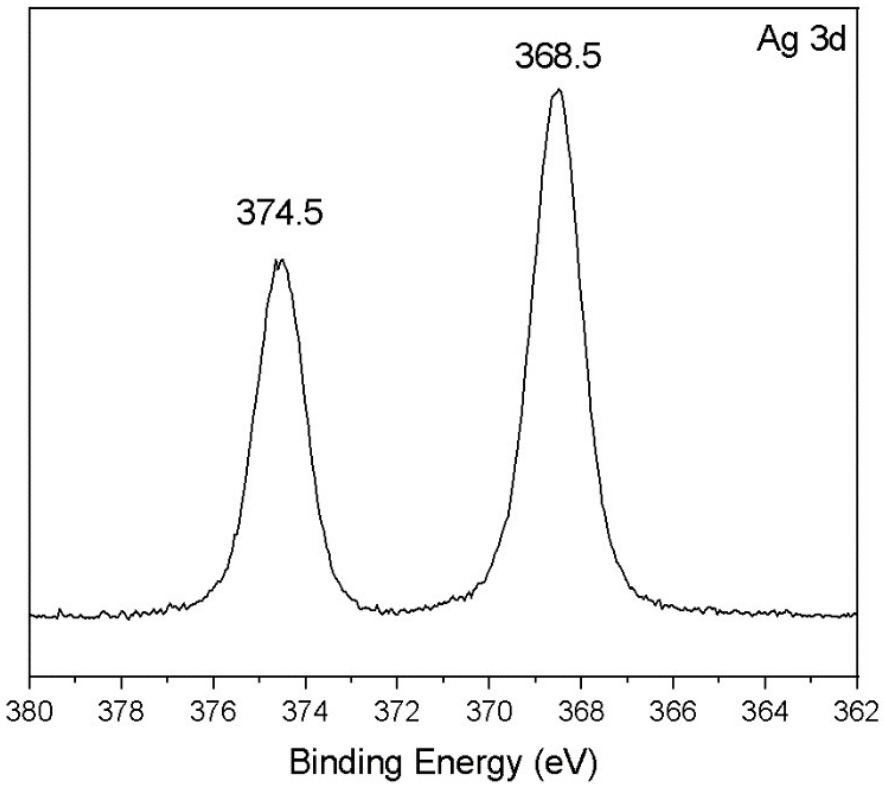


Fig. S9 Ag 3d XPS spectrum of $\mathbf{Ag_{11}}$.

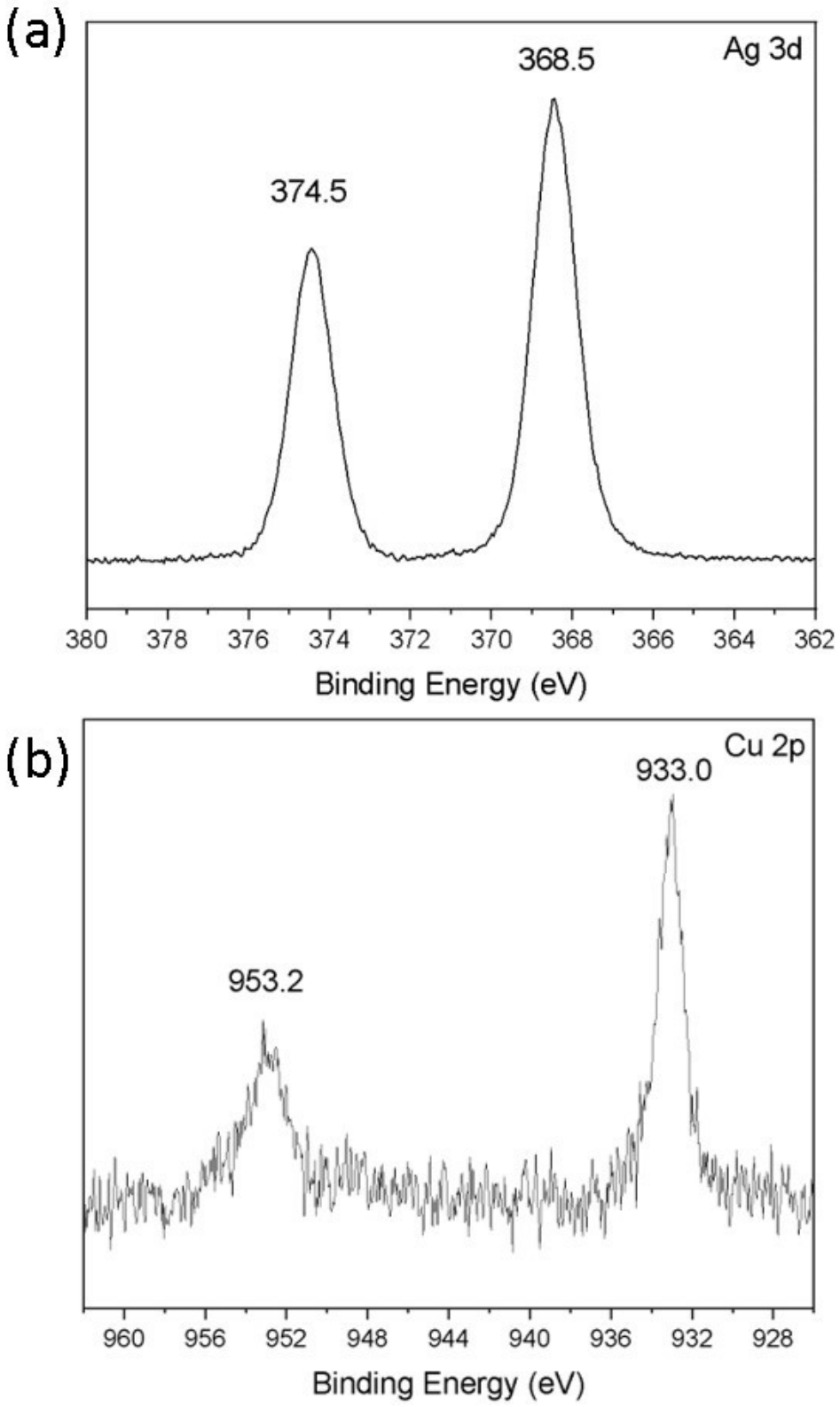


Fig. S10 (a) Ag 3d and (b) Cu 2p XPS spectra of $\mathbf{Cu_xAg_{11-x}}$.

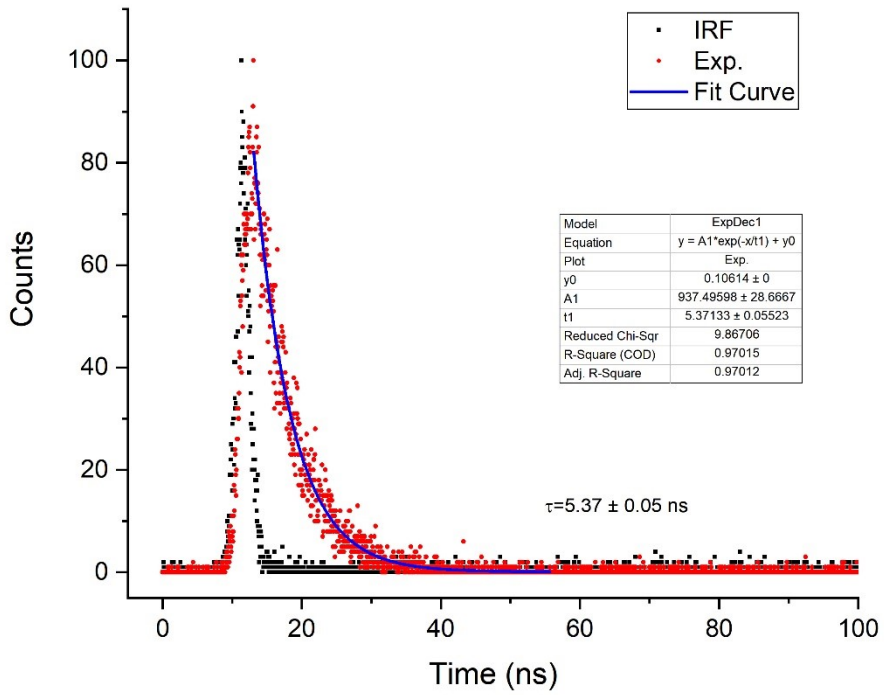


Fig. S11 The photoluminescence decay curve of **Ag_{11}** in 2-MeTHF at RT.

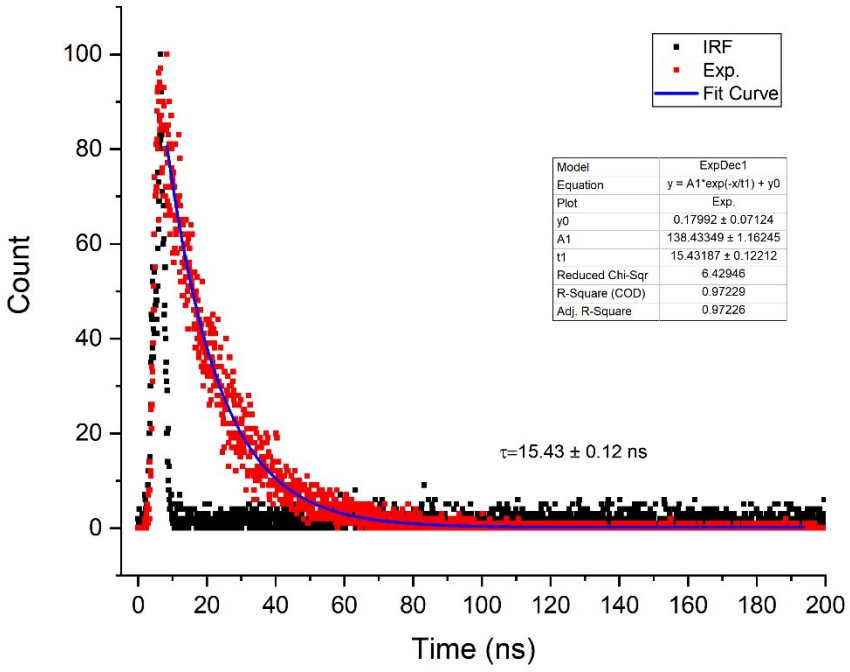


Fig. S12 The photoluminescence decay curve of **Ag_{11}** in 2-MeTHF at 77K.

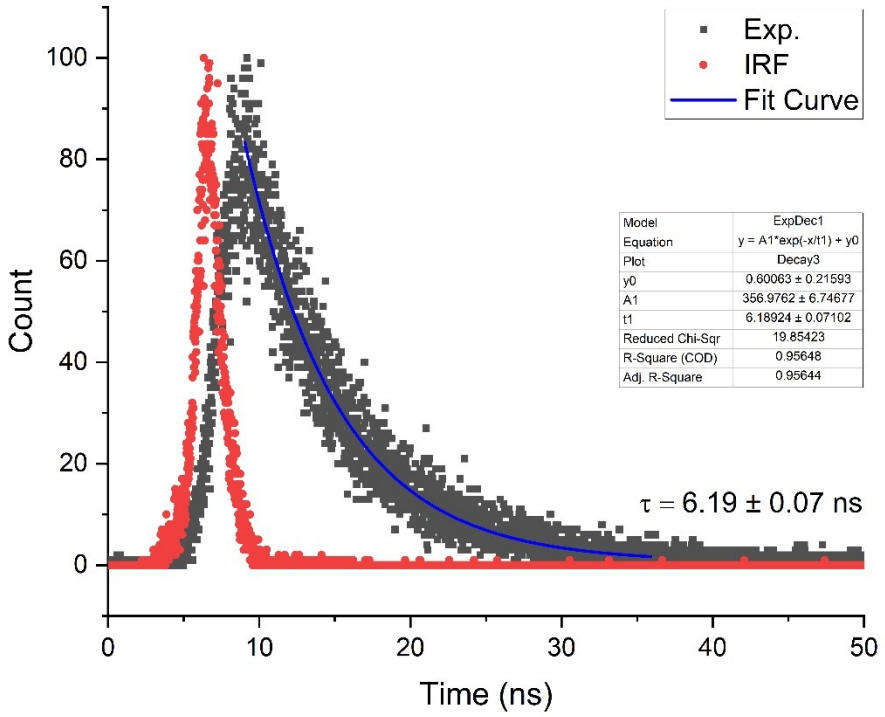


Fig. S13 The photoluminescence decay curve of Cu_xAg_{11-x} in 2-MeTHF at RT.

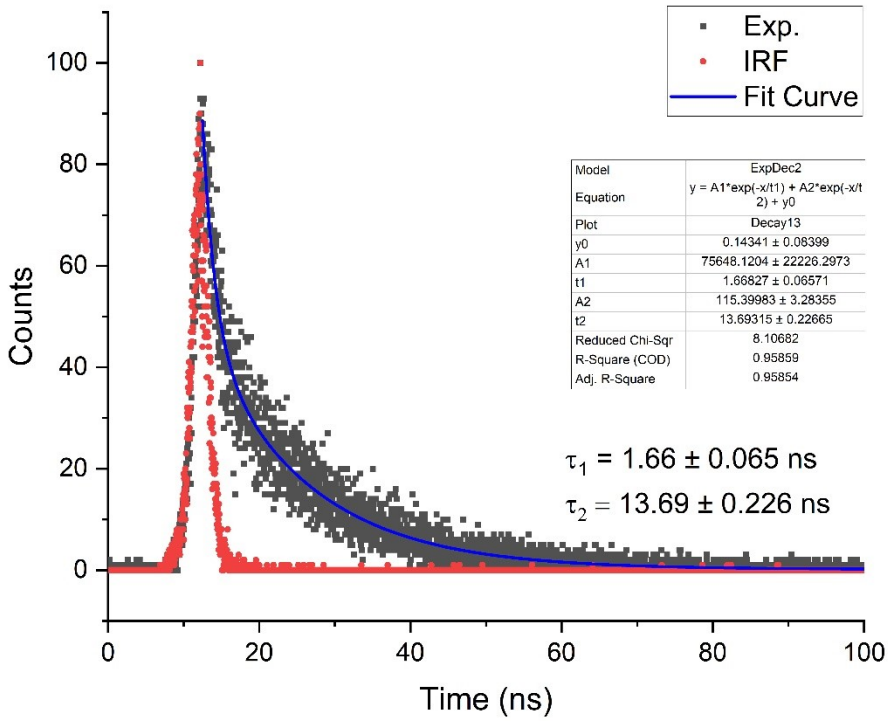


Fig. S14 The photoluminescence decay curve of Cu_xAg_{11-x} in 2-MeTHF at 77K.

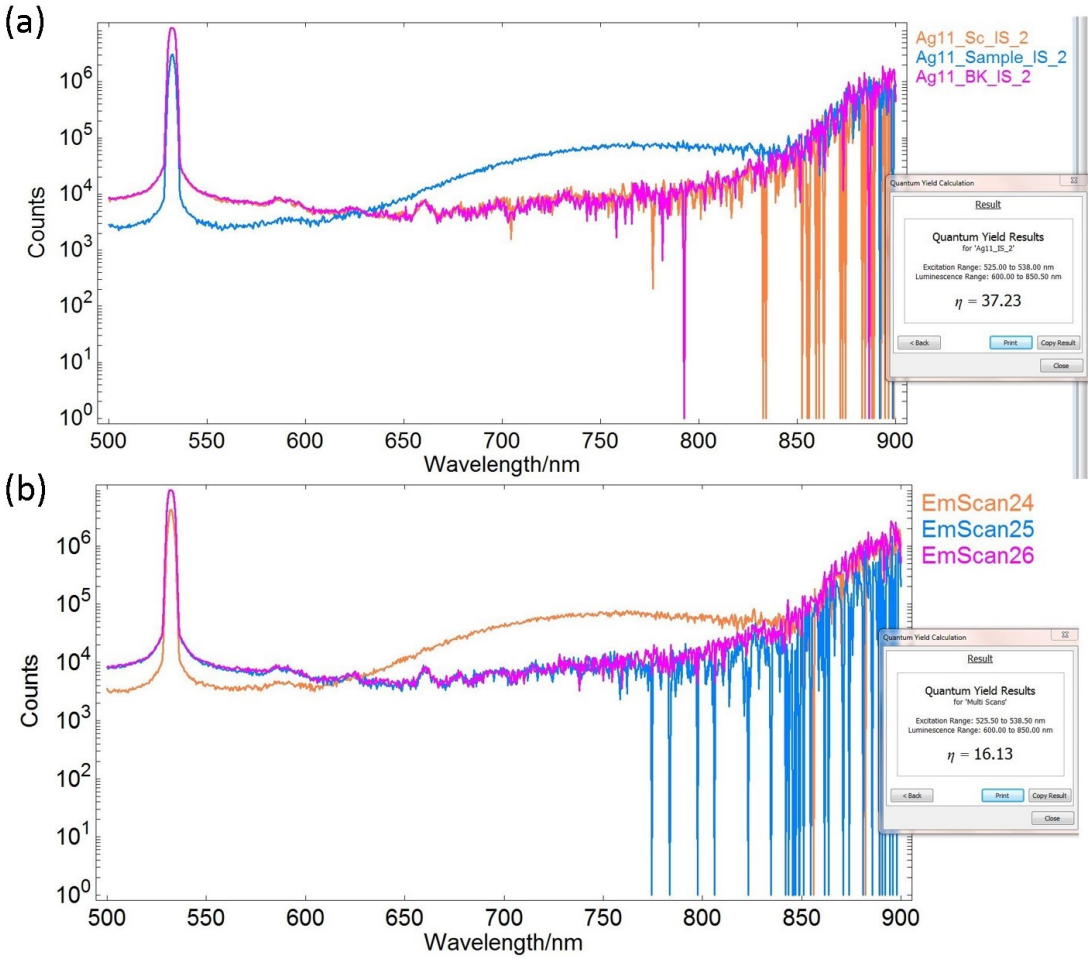
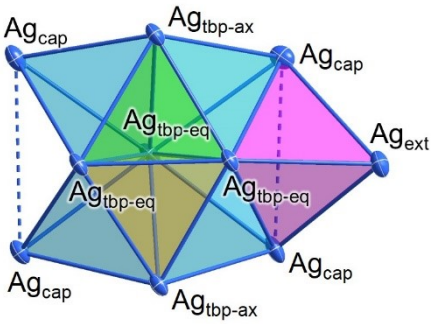


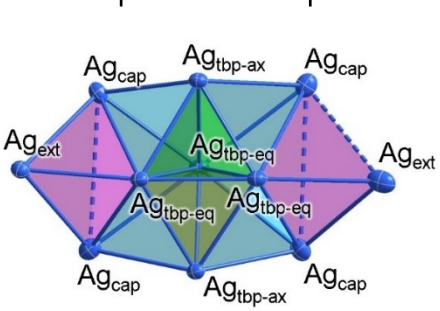
Fig. S15 (a) The photoluminescence quantum yield of $\mathbf{Ag_{11}}$ and (b) $\mathbf{Cu_xAg_{11-x}}$ in film state at ambient temperature.

Table S1 Selected bond lengths (Å) in **Ag_{10}** and **Ag_{11}**.

Compound	Tetrahedron edge yellow (Å)	Tetrahedron edge green (Å)	Tetrahedron edge cyan (Å)	Tetrahedron edge magenta (Å)	Tetrahedron height yellow (Å)	Tetrahedron height green (Å)	Tetrahedron height cyan (Å)	Tetrahedron height magenta (Å)
Ag_{10}	2.7985(13)	2.7848(14)	2.8437(14)	2.9116(14)	2.283	2.276	2.334	2.353 [3]
	2.8369(13)	2.8369(13)	2.8549(12)	3.0570(13)	2.313	2.339	2.382	2.400
	2.8437(14)	2.8464(12)	2.9567(13)	3.0967(15)	2.344	2.343	2.402	2.688
	2.8464(12)	2.8549(12)	3.0290(13)	3.0984(14)	2.377	2.360	2.548	2.731
	2.8549(12)	2.8896(13)	3.0483(13)	3.1355(13)	avg. 2.329	avg. 2.330	avg. 2.417	avg. 2.543
	2.9567(13)	2.9192(13)	3.0557(13)	3.600(1)			2.347	
	avg. 2.8562(13)	avg. 2.8553(13)	avg. 2.9647(13)	avg. 3.150(1)			2.351	
			2.8549(12)				2.418	
			2.8896(13)				2.530	
			2.9192(13)				avg. 2.412	
			2.9565(13)				2.283	
			3.0193(14)				2.356	
			3.1315(15)				2.376	
			avg. 2.9618(13)				2.437	
			2.7985(13)				avg. 2.363	
			2.8366(13)				2.309	
			2.8464(12)				2.340	
			2.9518(15)				2.389	
			2.9567(13)				2.577	
			3.0984(14)				avg. 2.404	
			avg. 2.9147(13)				avg. 2.399 [2]	
			2.7848(14)					
			2.8464(12)					
			2.9192(13)					
			2.9849(14)					
			3.0685(14)					
			3.1355(13)					
			avg. 2.9566(13)					
			avg. 2.9495(13) [1]					
Ag_{11}	2.7917(7)	2.7686(7)	2.7686(7)	3.0098(9)	2.291	2.277	2.268	2.289
	2.8017(7)	2.8326(7)	2.8407(7)	3.0758(8)	2.301	2.316	2.323	2.619 [3]
	2.8326(7)	2.8365(7)	2.9080(7)	3.2166(8)	2.307	2.317	2.449	2.834
	2.8365(7)	2.8407(7)	3.0136(8)	3.3783(9)	2.351	2.351	2.699	2.970
	2.8407(7)	2.8453(7)	3.2026(8)	3.4723(8)	avg. 2.313	avg. 2.315	avg. 2.435	avg. 2.678
	2.9003(7)	2.9080(7)	3.2957(8)	3.9802(9)			2.303	2.375 [3]
	avg. 2.8339(7)	avg. 2.8386(7)	avg. 3.0049(8)	avg. 3.3555(9)			2.347	2.386
			2.8017(7)	2.9219(7)			2.379	2.718
			2.8407(7)	3.0787(7)			2.547	2.848
			2.9003(7)	3.1093(8)			avg. 2.394	avg. 2.582
			2.9507(8)	3.2026(8)			2.280	avg. 2.630 [4]
			3.0514(8)	3.2170(7)			2.335	
			3.1093(8)	3.7852(9)			2.433	
			avg. 2.9424(8)	avg. 3.2191(8)			2.706	
			2.8326(7)	avg. 3.2873(8)			avg. 2.439	
			2.8453(7)				2.302	
			2.9080(7)				2.342	
			2.9155(7)				2.414	
			3.0758(8)				2.549	



			3.1519(8)				avg. 2.402	
			avg. 2.9549(7)				avg. 2.417 [2]	
			2.7917(7)					
			2.8326(7)					
			2.9003(7)					
			3.0238(7)					
			3.2166(8)					
			3.2907(8)					
			avg. 3.0093(7)					
			avg. 2.9778(7) [1]					



Colored background represents the average bond distances. [1] The average bond length of all cyan tetrahedrons. [2] The average height of all cyan tetrahedrons. [3] Distances from Ag_{ext} to $\Delta Ag_{tbp\text{-}eq}$-$Ag_{cap}$–$Ag_{cap}$. [4] The average height of all magenta tetrahedrons. Red text represents the Ag…Ag distances are longer than their sum of vdW radii (3.44 Å).

Table S2 Selected X-ray crystallographic data of **Ag_{11}**.

Compound	**Ag_{11}** · 2(CH_2Cl_2)
CCDC no.	2287343
Chemical formula	$C_{51}H_{116}Ag_{11}Cl_4F_3O_{19}P_8S_{17}$
Formula weight	3211.58
Wavelength, Å	0.71073
Crystal System	Monoclinic
Space group	$P2_1/c$
a, Å	21.1314(12)
b, Å	20.6403(11)
c, Å	25.9515(14)
α, deg.	90
β, deg.	110.450(2)
γ, deg.	90
V, Å^3	10605.6(10)
Z	4
Temperature, K	100(2)
ρ_{calcd}, g/cm^3	2.011
μ, mm^{-1}	2.596
θ_{max}, deg.	25.00
Completeness, %	98.9
Reflection collected / unique	60351 /18458 [*R*(int) = 0.0413]
Restraints / parameters	402 / 1110
[a] *R*1, [b] *wR*2 [I > 2σ(I)]	0.0426, 0.1023
[a] *R*1, [b] *wR*2 (all data)	0.0576, 0.1128
GOF	1.053
Largest diff. peak and hole, e/Å^3	2.864 and -2.017

[a] $R1 = \Sigma \left| \left| F_o \right| - \left| Fc \right| \right| / \Sigma \left| F_o \right|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Measurement of Quantum Yield

The quantum yield of **Ag_{11}** and **Cu_xAg_{11-x}** was determined by a comparative method. Absolute values are calculated by using $[Ru(bpy)_3]^{2+}$ as the standard sample according to the following equation:[S1,S2]

$$\Phi_a = \frac{\frac{F_a}{A_a} \times \eta_a^2}{\frac{F_s}{A_s} \times \eta_s^2} \times \Phi_s$$

Where the subscripts "s" and "a" denote standard and analyte, respectively. Φ is the emission quantum yield. F is the integrated emission intensity. A is the absorbance. η is the refractive index of the solvent. The quantum yield for **Ag_{11}** was determined by averaging results from three separate experiments, using $[Ru(bpy)_3]^{2+}$ in alcohol as a standard reference. The quantum yield for **Cu_xAg_{11-x}** was calculated based on an average from two experiments, with $[Ru(bpy)_3]^{2+}$ dissolved in water serving as the standard. To prepare the PMMA film, 2 mg of **Ag_{11}** (or 2 mg of **Cu_xAg_{11-x}**) was mixed with a PMMA solution in CH_2Cl_2 and stirred until evenly distributed. The mixture solution was then dropped onto a quartz template and left to dry, forming a film.

References:

S1. G. A. Crosby and J. N. Demas, *J. Am. Chem. Soc.*, 1970, **92**, 7262–7270.

S2. G. A. Crosby and J. N. Demas, *J. Am. Chem. Soc.*, 1971, **93**, 2841–2847.

Table S3 Determination of photoluminescence quantum yield of **Ag_{11}** and **Cu_xAg_{11-x}**.

	solvent	Absorbance (A)	Integrated emission intensity (F)	F/A (*10^{12})	Quantum Yield (Φ)	Average Quantum Yield (Φ)	Film Quantum Yield ($Φ_{Film}$)
$[Ru(bpy)_3]^{2+}$	Alcohol[a]	0.7076	1.570E+12	2.21			
$[Ru(bpy)_3]^{2+}$	Alcohol[a]	0.7034	1.568E+12	2.229	0.089[b][c]	0.089[b][c]	
$[Ru(bpy)_3]^{2+}$	Alcohol[a]	0.6828	1.247E+12	1.826			
Ag_{11}	2-MeTHF	0.8156	2.81E+12	3.45	0.153[c]		
Ag_{11}	2-MeTHF	0.7885	2.814E+12	3.57	0.157[c]	0.146[c]	0.372[d]
Ag_{11}	2-MeTHF	0.8291	1.975E+12	1.826	0.129[c]		

	solvent	Absorbance (A)	Integrated emission intensity (F)	F/A (*10^{8})	Quantum Yield (Φ)	Average Quantum Yield (Φ)	Film Quantum Yield ($Φ_{Film}$)
$[Ru(bpy)_3]^{2+}$	H_2O	0.0867	6.42E+8	74.09	0.063 [c][e]	0.063[c][e]	
$[Ru(bpy)_3]^{2+}$	H_2O	0.0854	6.04E+8	70.72			
Cu_xAg_{11-x}	2-MeTHF	0.0645	8.12E+8	83.13	0.080[c]	0.078[c]	0.161[d]
Cu_xAg_{11-x}	2-MeTHF	0.0636	8.18E+8	78.34	0.075[c]		

[a] ethanol-methanol (v/v = 4:1). [b] *J. Chem. Soc., Perkin Trans. 2,* 1984, 1293-1301. [c] Degas. [d] PLQY was determined with the complexes in plastic (PMMA film) through an integrating sphere on FLS920 spectrometer. [e] *Phys. Chem. Chem. Phys.*, 2009, **11**, 9850-9860.