Supporting Information

Temperature dependent molecular fluorescence of $[Ag_m]^{n+}$ quantum clusters stabilized by phosphate glass networks

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Mass spectra analysis details:

We firstly get the mass spectra of silver doped/undoped glass samples, H_2O and dilute hydrochloric acid. Then, compared with H_2O and dilute hydrochloric acid, the characteristic peaks of the silver doped glass samples were identified as two groups of peaks (*m*/*z* = -354; -355; -356; -357; -358; -359 and *m*/*z* = -439; -440; -441; -442; -443; -444) with almost fixed $\Delta m/z$=1 between adjacent peaks. The *m/z*=1 gap among the mass spectra peaks are generated from isotopes of Ag and Zn with Δm = 2 (Table S3, S4). Accordingly, the molecular fragments charge was evaluated as -2. Subsequently, to further determine the fluorophosphate coordinated molecule fragment, we compiled a small program to compute all possible $[nAg^{+}(m\text{-}n)Ag^{0}][P_xZn_yO_zF_w]\cdot aH^{+}\cdot bOH^{-}\cdot cH_2O$ configuration with n = (0~10), m = (1~20), x = (2~32), y = (0~10), z = (6~160), w = (0~20), a = (1~50), b = (1~50), c = (1~20). We started the program to match the strongest peaks (*m*/*z* = -356 and *m*/*z* = -442) by using the most abundant isotope (^{107}Ag; ^{64}Zn), after that we can extend the program selected $[nAg^{+}(m\text{-}n)Ag^{0}][P_xZn_yO_zF_w]\cdot aH^{+}\cdot bOH^{-}\cdot cH_2O$ configurations to all the other mass-to-charge ratio of the characteristic peaks within the same m/z group. To a further step, according to phosphate glass structure that $[P(O, F)_4]$ connect into chain structure and $[ZnO_4]$ tetrahedral units in the investigated P_2O_5-ZnF_2-Ag glass, we excluded unreasonable configurations, such as:

$[Ag_2(H_2O)_1(P_3Zn_3O_{12}F_0H_0)]^{2-}$ (m/z = -356);

$[Ag_2(H_2O)_2(P_4Zn_1O_{11}F_5H_1)]^{2-}$ (m/z = -356);

$[Ag_5(H_2O)_0(P_3Zn_1O_{12}F_0H_2)]^{2-}$ (m/z = -442);

$[Ag_4(H_2O)_3(P_3Zn_1O_7F_5OH_2)]^{2-}$ (m/z = -442);

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Finally, $[Ag_2(H_2O)_2(P_4Zn_1O_{11}F_5H_1)]^{2-}$ (m/z = -356) and $[Ag_4(H_2O)_3(P_4O_{11}F_5H_3)]^{2-}$ (m/z = -442), as shown in Figure 4c-d, were finally worked out as the highly possible molecular fragments containing $[Ag_2]^{2+}$ and $[Ag_4]^{2+}$ configurations, respectively.

Table S1 Glass transition (T_g), crystallization peak (T_c), melting temperature (T_m) and glass stability (Δ*T*) for different glass formulations.

Glass	T_g(℃)	T_c(℃)	T_m(℃)	$\Delta T=(T_g-T_c)$℃
P0Ag	464	615	765	151
P0.4Ag	478	609	762	131
P0.8Ag	465	602	758	137
P1.2Ag	450	598	752	148
P1.6Ag	452	596	743	144
P2Ag	443	591	761	148
P_2O_5-MgO-CaO-Na_2O[1]	448	554	764	106

1. M. T. Islam, N. Sharmin, G. A. Rance, J. J. Titman and I. Ahmed, *Journal of Biomedical Materials Research Part B Applied Biomaterials*, 2019.

Table S2 The proportion of Q^2 tetrahedra and Q^1 tetrahedra of ^{31}P NMR spectra (Figure

1c) calculated by 2-Gaussian fit curves.

Name	P0.4Ag	P0.8Ag	P1.2Ag	P1.6Ag	P2Ag
Q^1 (%)	40.7	38.2	39.2	39.0	38.4
Q^2 (%)	59.3	61.8	60.8	61.0	61.6

Table S3 Isotopes of zinc and their proportion.

Zn	^{64}Zn	^{66}Zn	^{67}Zn	^{68}Zn
Proportion	48.6%	27.9%	4.1%	18.8%

Table S4 Isotopes of silver and their proportion.

Ag	^{107}Ag	^{109}Ag
Proportion	51.8%	48.2%

Table S5 The lifetimes (τ) and the standard deviation (σ) of $[Ag_4]^{2+}$ QCs (λ_{ex} = 375 nm, λ_{em} = 390 nm) in P1.6Ag from 78K to 450K.

Temperature/K	Lifetime/ns
78	4.057±0.008
90	4.145±0.016
105	4.055±0.010
120	4.052±0.014
135	4.081±0.011
150	4.003±0.017
165	3.936±0.007
180	4.000±0.008
195	3.964±0.012
210	3.785±0.004
225	3.774±0.008
240	3.879±0.012
255	3.861±0.002
270	3.858±0.010
285	3.886±0.007
300	3.685±0.008
315	3.710±0.009
330	3.676±0.020
345	3.634±0.002
360	3.670±0.006
375	3.541±0.008
390	3.486±0.004
405	3.277±0.003
420	3.057±0.011
435	2.936±0.004
450	2.816±0.009

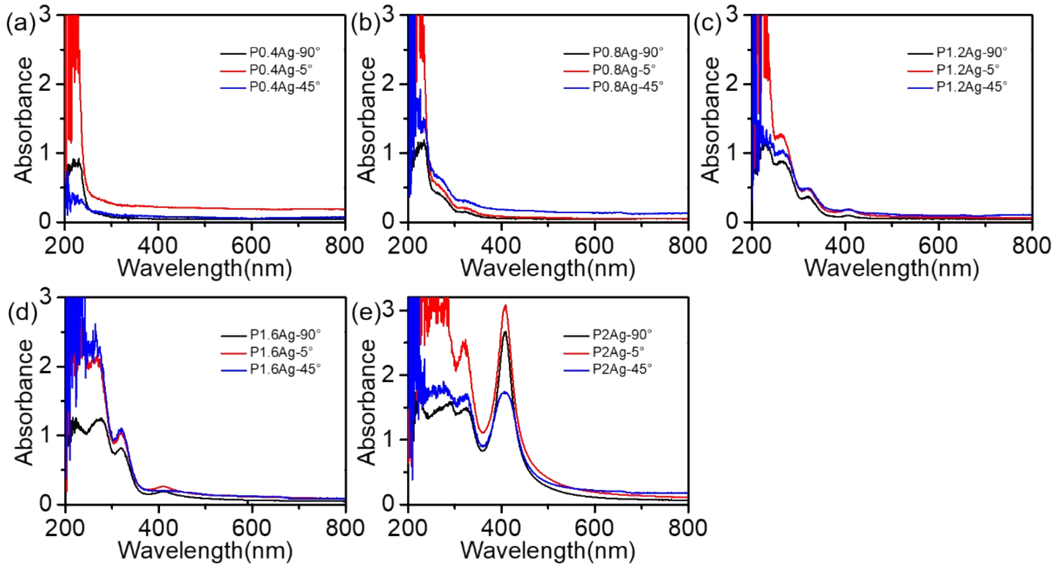

Figure S1 Absorption spectra of $60PO_{2/5}$-$40ZnF_2$-xAg glasses measured with different light incident angles (90°, 45°, 5°): (a)P0.4Ag; (b)P0.8Ag; (c)P1.2Ag; (d)P1.6Ag; (e)P2Ag.

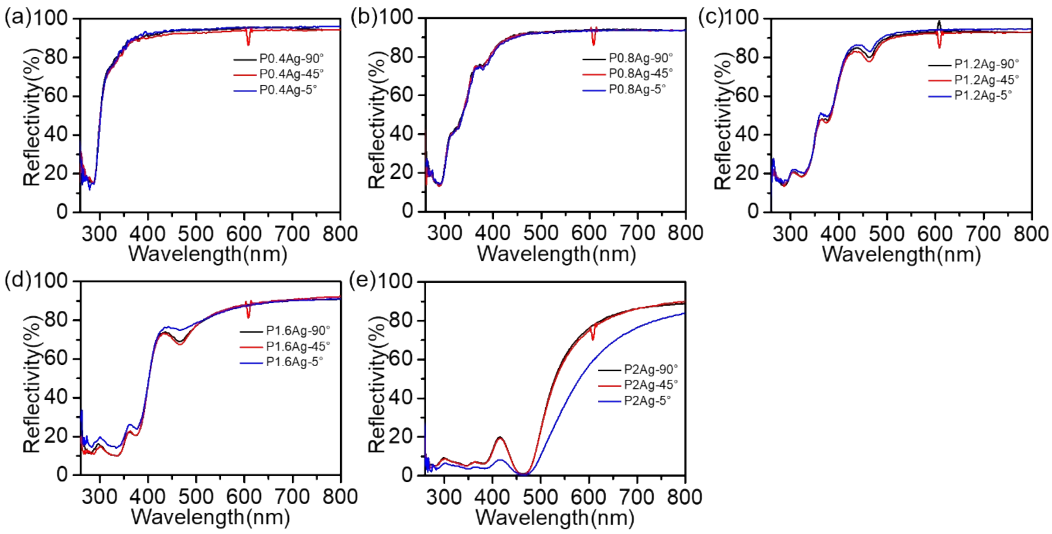

Figure S2 Reflection spectra of $60PO_{2/5}$-$40ZnF_2$-xAg glasses measured with different light incident angles (90°, 45°, 5°): (a)P0.4Ag; (b)P0.8Ag; (c)P1.2Ag; (d)P1.6Ag; (e)P2Ag.

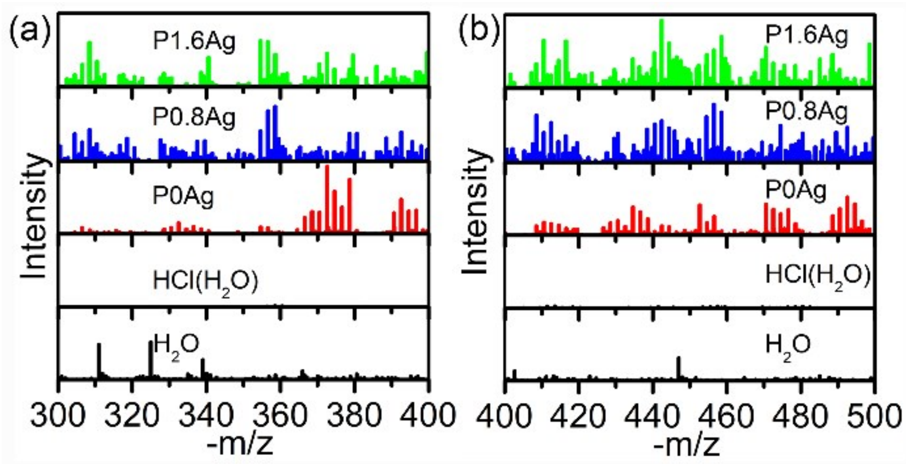

Figure S3 Mass spectrum of P*x*Ag (x = 0, 0.8, 1.6) and H_2O, HCl (H_2O): (a) m/z range: -300 ~ -400, (b) m/z range: -400 ~ -500.

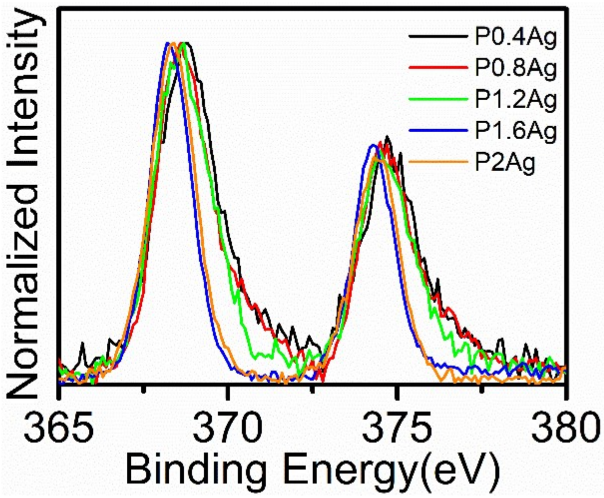

Figure S4 Ag $3d_{5/2}$ X-ray photoelectron spectra (XPS) spectra of P_2O_5-ZnF_2-*x*Ag glasses.

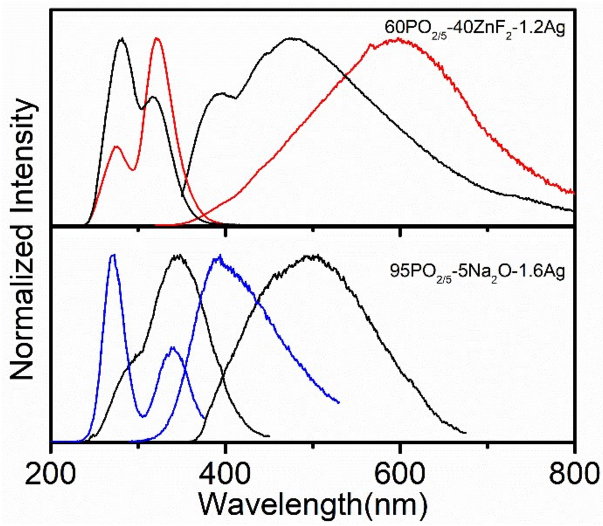

Figure S5 Normalized fluorescence spectra of different silver species in $95PO_{2/5}$-$5Na_2O$-1.6Ag glass and $60PO_{2/5}$-$40ZnF_2$-1.2Ag glass.

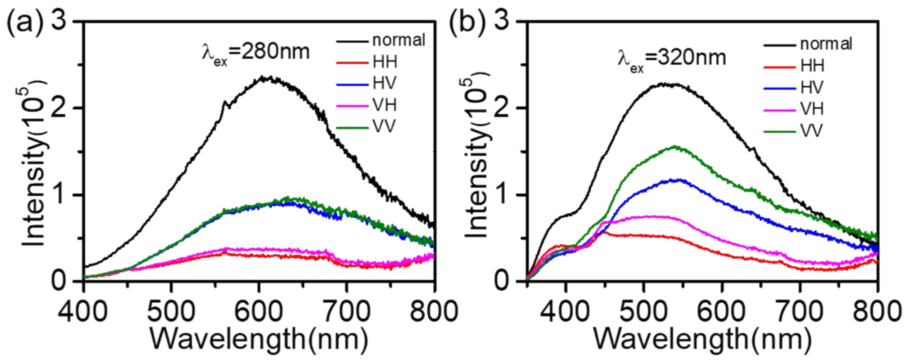

Figure S6 Polarized spectra of $60PO_{2/5}$-$40ZnF_2$-1.6Ag glasses: (a) λ_{ex} = 280nm; (b) λ_{ex} = 320nm.

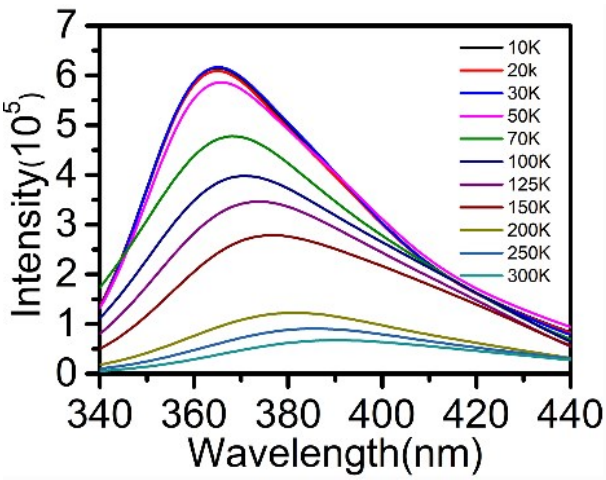

Figure S7 The fitted $S_1 \rightarrow S_0$ emission by a Gaussian multi-peak decomposition method from the total emission excited at 320nm of $[Ag_4]^{2+}$ QCs in P1.6Ag from 10K to 300K.