## **Supporting information**

## The spectral relaxation dynamics and the molecular crowding effect of the silver nanoclusters synthesized in the polymer scaffold

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Figure  $S_1$ : The power density and the spectra of the LED lamps used for synthesizing the PMAA-AgNCs



Figure  $S_2$ : The (a) fluorescence decay dynamics and the (b) spectral relaxation dynamics of the PMAA-AgNCs in the glycerol solution. The excitation wavelength is fixed at 510 nm, and the reconstructed time-resolved emission spectra of the PMAA-AgNCs are indicated in the inset.



Figure  $S_3$ : The (a) fluorescence decay dynamics and the (b) spectral relaxation dynamics of the PMAA-AgNCs embedded in the PVA film. The excitation wavelength is fixed at 510 nm, and the reconstructed time-resolved emission spectra of the PMAA-AgNCs are indicated in the inset.



Figure  $S_4$ : The (a) fluorescence decay dynamics and the (b) spectral relaxation dynamics of the PMAA-AgNCs solid powder. The excitation wavelength is fixed at 510 nm, and the reconstructed time-resolved emission spectra of the PMAA-AgNCs are indicated in the inset.



Figure  $S_5$ : The (a) fluorescence decay dynamics and the (b) spectral relaxation dynamics of the PMAA-AgNCs in the acetate buffer. The excitation wavelength is fixed at 445 nm, and the reconstructed time-resolved emission spectra of the PMAA-AgNCs are indicated in the inset.



Figure  $S_6$ : The (a) fluorescence decay dynamics and the (b) spectral relaxation dynamics of the PMAA-AgNCs in the MES buffer. The excitation wavelength is fixed at 445 nm, and the reconstructed time-resolved emission spectra of the PMAA-AgNCs are indicated in the inset.



Figure  $S_7$ : The anisotropy decay dynamics of PMAA-AgNCs (a) solid powder (b) embedded in the PVA film.



Figure  $S_8$ : The relative fluorescence intensity of the PMAA-AgNCs in AOT, CTAB and Triton X-100 RMs



Figure S<sub>9</sub>: The (a) fluorescence decay dynamics and the (b) spectral relaxation dynamics of the PMAA-AgNCs in 40% PEG 400 solution. The excitation wavelength is fixed at 510 nm, and the reconstructed time-resolved emission spectra of the PMAA-AgNCs are indicated in the inset.



Figure  $S_{10}$ : The (a) fluorescence decay dynamics and the (b) spectral relaxation dynamics of the PMAA-AgNCs in the Triton X-100 RMs. The excitation wavelength is fixed at 510 nm, and the reconstructed time-resolved emission spectra of the PMAA-AgNCs are indicated in the inset.



$\lambda_{excitation}$	510 nm							445 nm	
	MES buffer	Acetate buffer	Glycerol	40% PEG 400	TX-100 RMs	PVA film	powder	MES buffer	Acetate buffer
Concentration/M	3.8×10 <sup>-4</sup>	N.A.	N.A.	3.8×10 <sup>-4</sup>	3.8×10 <sup>-4</sup>				
$v(0)/cm^{-1}$	16196	16642	16749	16473	16323	16160	16128	17303	18123
$v(\infty)/cm^{-1}$	15592	16323	16025	15806	15765	13900	13712	15527	16702
$^{a}\Delta v/cm^{-1}$	604	319	724	667	558	2260	2416	1776	1421
$a_1$	1.00	0.24	0.12	0.22	0.28	0.77	0.65	0.05	0.12
a <sub>2</sub>	N.A.	0.76	0.88	0.78	0.72	0.23	0.35	0.95	0.88
$ au_1/ns$	1.4	0.27	0.2	0.2	0.3	0.77	0.28	0.05	0.05
$\tau_2/ns$	N.A.	1.5	2.1	2.1	2.5	3.4	1.9	1.3	1.2
${}^{b}\tau_{average}/ns$	1.4	1.2	1.9	1.7	1.9	1.4	0.8	1.2	1.1

## Table S<sub>1</sub>: The fitting parameters of the spectral relaxation dynamics of PMAA-AgNCs in various environments

 $^{a}\Delta v = v(0) - v(\infty)$ 

 ${}^{b}\tau_{average} = (a_2 \times \tau_1 + a_2 \times \tau_2)/(a_{1+}a_2)$