## **Supplementary Information**

## Solvatofluorochromism of polyethyleneimine-encapsulated Ag nanoclusters and their concentration-dependent fluorescence

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**Fig. S1** UV-vis (a) and fluorescence spectra (b) of PEI-capped Ag nanoclusters dispersed in water, methanol, ethanol, ethylene glycol, n-propanol, and isopropanol.



**Fig. S2** Time evolution of UV-vis (a) and fluorescence spectra (b) of PEI-capped Ag nanoclusters dispersed in DMSO.



**Fig. S3** Time evolution of UV-vis (a) and fluorescence spectra (b) of PEI-capped Ag nanoclusters dispersed in THF.



**Fig. S4** Comparison of the changes of fluorescence intensity of PEI-capped Ag nanoclusters dispersed in other water-organic mixtures at different ratios.



Fig. S5 Comparison the stability of PEI-capped Ag nanoclusters dispersed in different solvents.



**Fig. S6** Comparison of the absorption, excitation and emission spectra of different concentration of PEI-capped Ag nanoclusters (a, 1%; b, 20%; c, 100%).

Solvent	Solubility of AgNCs	Solubility of PEI	Е	п	QY (%)
water	Good	Good	78.5	1.333	2.5
methanol	Good	Good	32.7	1.329	3.2
ethanol	Good	Good	24.5	1.362	3.8
ethylene glycol	Good	Fair	37.7	1.431	3.7
n-propanol	Good	Fair	20.3	1.399	4.3
isopropanol	Good	Fair	18.62	1.378	3.0
acetonitrile	Good	Fair	37.5	1.344	3.3
DMF	Good	Fair	36.7	1.428	4.2
DMSO	Good	Fair	46.45	1.478	2.9
THF	Fair	Insoluble	7.6	1.405	1.8
EGME (15 min)	Good	Fair	16.9	1.402	2.4
EGME (180 min)	Good	Fair	-	_	0.8

**Table S1** Solubility and quantum yield (QY) of PEI-capped Ag nanoclusters (AgNCs) and solubility of pure PEI in different solvents and the corresponding solvent constants.

Note that  $\varepsilon$  and n are the dielectric constant of the solvent and its refractive index, respectively (at 20 °C).