

## Electronic Supplementary Information

### **Aggregation, dissolution and cyclic regeneration of Ag nanoclusters based on pH-induced conformational changes of polyethyleneimine template in aqueous solutions**

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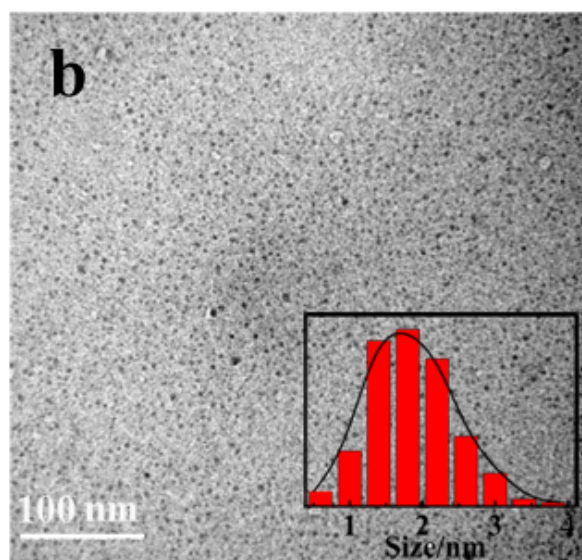
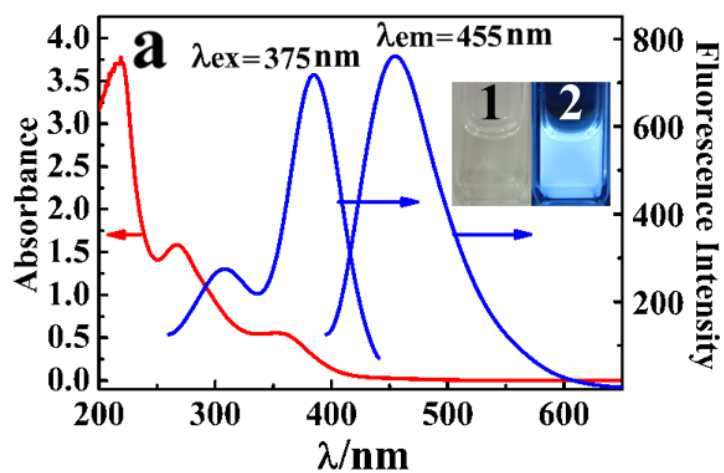
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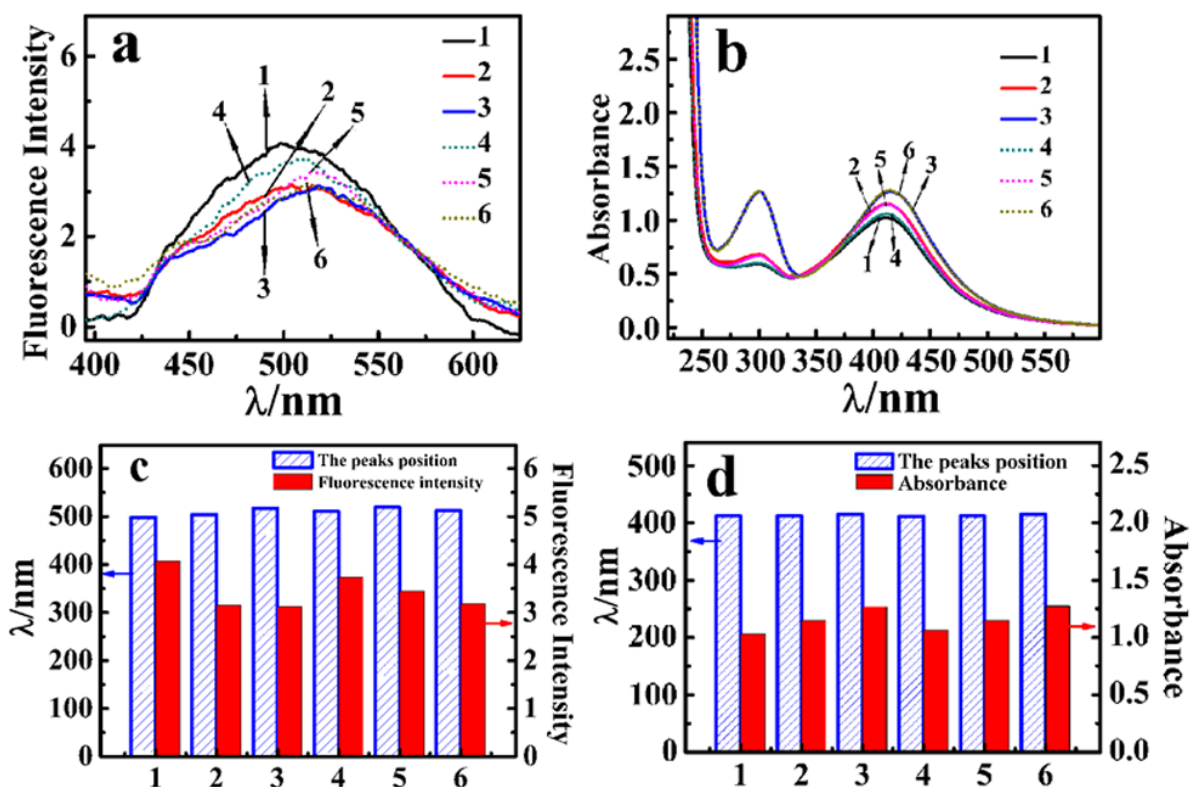
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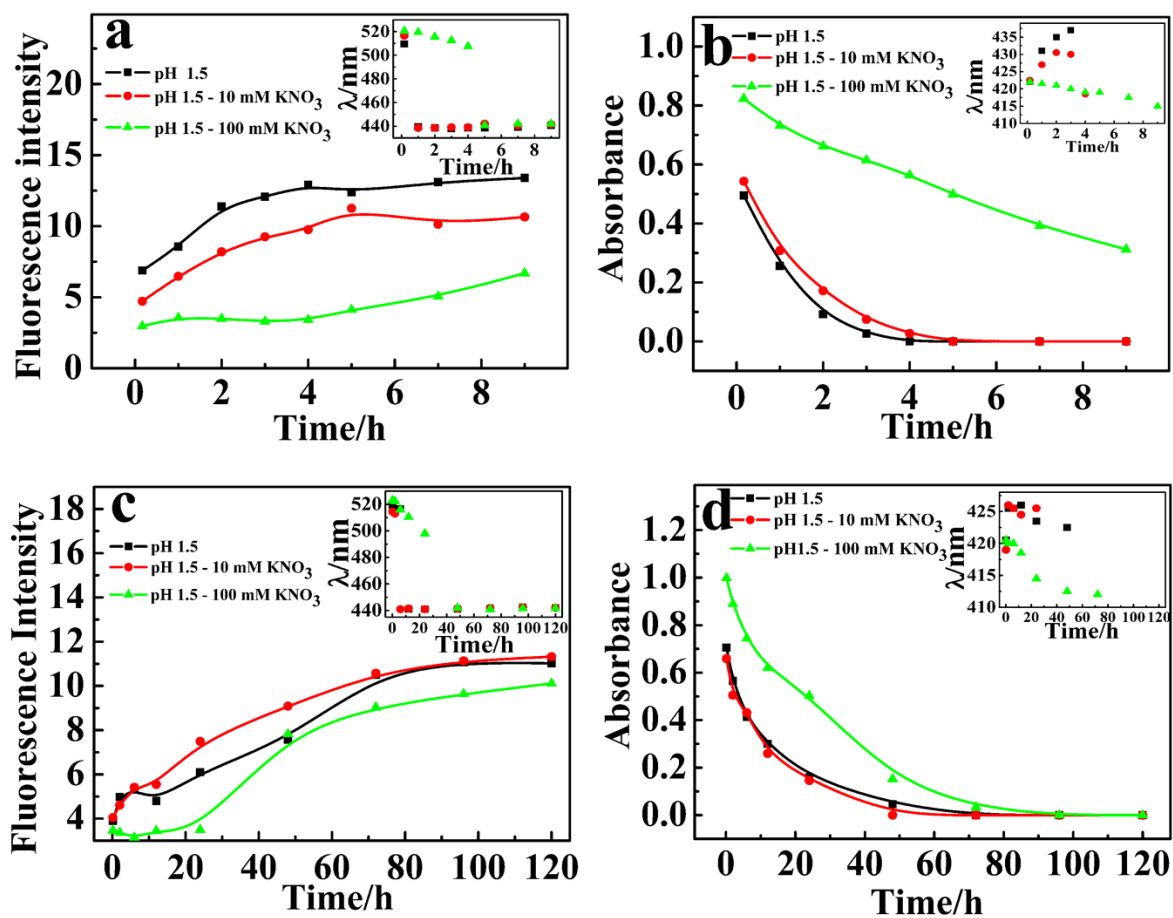
E-mail addresses: linb@swu.edu.cn(N.B. Li); luohq@swu.edu.cn (H.Q. Luo).



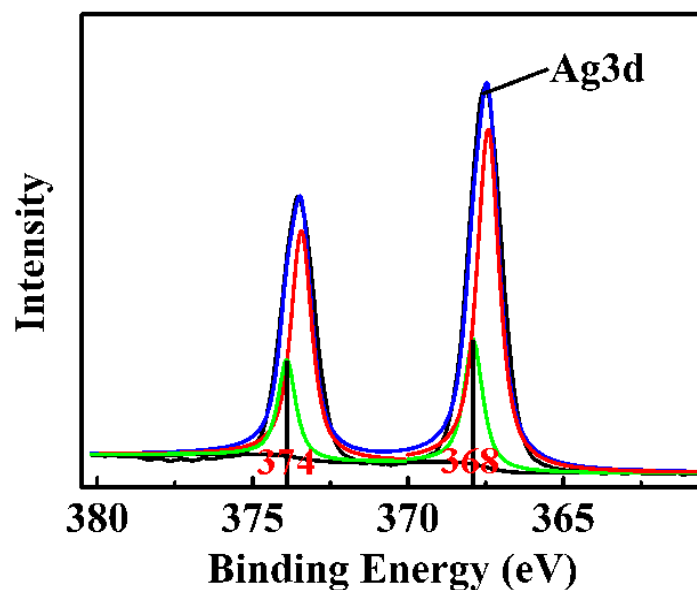
**Fig. S1** (a): Fluorescence and UV-vis absorption spectra of PEI-templated silver nanoclusters (PEI-AgNCs). The inset is the photographs of PEI-AgNCs solutions diluted 100-fold with distilled water under visible light (no. 1) and UV light (no. 2). (b) TEM image of PEI-AgNCs. The inset shows the particle size distribution of PEI-AgNCs.



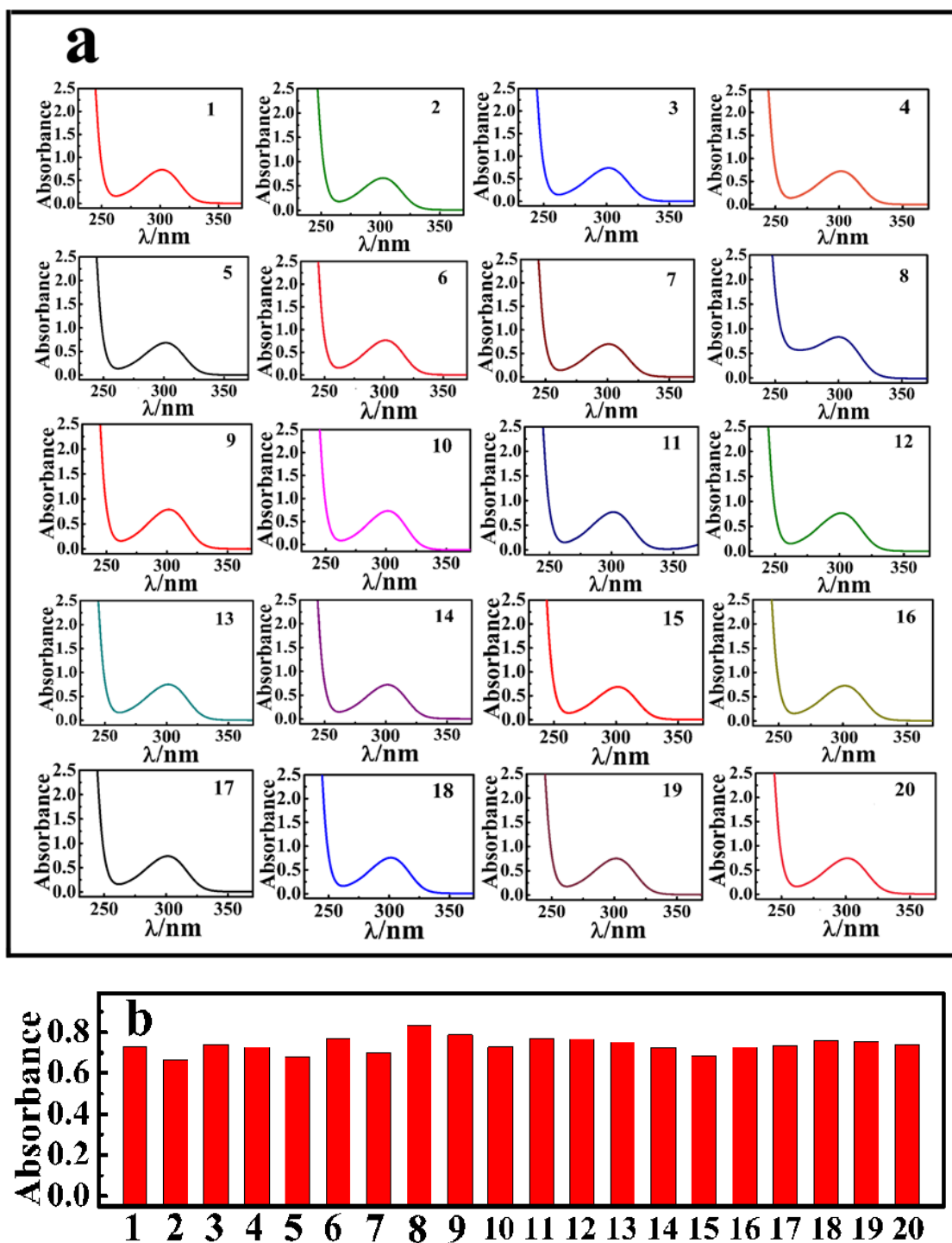
**Fig. S2** Influence of the ionic strength and concentration of dissolved oxygen on aggregation behavior of PEI-AgNCs. (a) Fluorescence and (b) UV-vis absorption spectra obtained instantly after PEI-AgNCs aggregation in 0 mM (no. 1 and 4), 10 mM (no. 2 and 5) and 100 mM (no. 3 and 6)  $\text{KNO}_3$  solution in air (no. 1, 2 and 3) and without air (no. 4, 5 and 6), respectively; (c) and (d) show the comparison of the site and intensity of corresponding fluorescence and UV-vis absorption peaks, respectively. As shown in Figure S2, eliminating oxygen had very little impact on the aggregation of PEI-AgNCs and formation of AgNPs. However, the evidences including weaker fluorescence intensity, stronger absorbance, and red shift of absorption peaks all indicated that higher ionic strength made the aggregation of PEI-AgNCs more obvious to some extent.



**Fig. S3** Changes of fluorescence intensity and absorbance of the solution with different ionic strengths over time in air (a and b) and without air (c and d), respectively. The insets show the corresponding change of peaks position over time.



**Fig. S4** X-ray photoelectron spectroscopy (XPS) spectra of AgNPs. The two binding energy peaks of Ag 3d were centered at 368 and 374 eV, which were consistent with the standard spectrum reported before.<sup>S1,S2</sup> However, it can be seen from Figure S4 that AgNPs sample seems to be mainly constructed with Ag (I). This result is largely attributed to the limited measuring depth in XPS measurements, and as we all know, the maximum measuring depth is only about 5 nm in XPS measurements. Because of the formation of an Ag<sub>2</sub>O film on the surface of AgNPs, X-ray photoelectron must first penetrate the Ag<sub>2</sub>O film before detecting Ag<sup>0</sup>, as the result, only a small portion of Ag<sup>0</sup> were explored by the XPS measurements in the AgNPs sample.

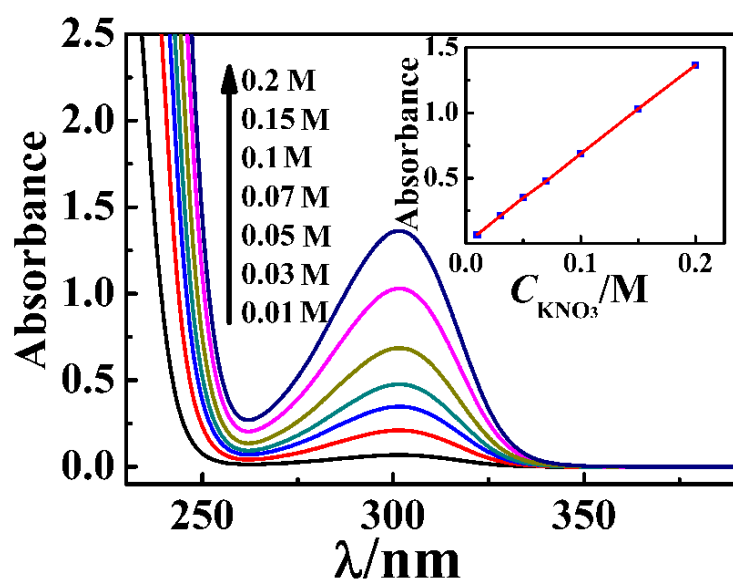


**Fig. S5** (a): UV-vis absorption spectra of nitric acid (no. 1), different types of nitrates (nos. 2→14 :  $\text{AgNO}_3$ ,  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{Y}(\text{NO}_3)_3$ ,  $\text{Al}(\text{NO}_3)_3$ ), and several kinds of nitrates mixtures selected randomly (nos. 15→20 : mixture of  $\text{NaNO}_3$  and  $\text{KNO}_3$ , of  $\text{KNO}_3$  and  $\text{Mg}(\text{NO}_3)_2$ , of  $\text{Mg}(\text{NO}_3)_2$  and  $\text{Ca}(\text{NO}_3)_2$ , of  $\text{Zn}(\text{NO}_3)_2$  and  $\text{Al}(\text{NO}_3)_3$ ), of  $\text{LiNO}_3$ ,  $\text{NaNO}_3$  and  $\text{Cd}(\text{NO}_3)_2$ , and of  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$  and  $\text{Al}(\text{NO}_3)_3$ ) in aqueous solution. All of which contain same concentration of  $\text{NO}_3^-$  (0.1 M). (b): Bar charts of the absorbance values of corresponding nitric acid and the nitrates mentioned above at

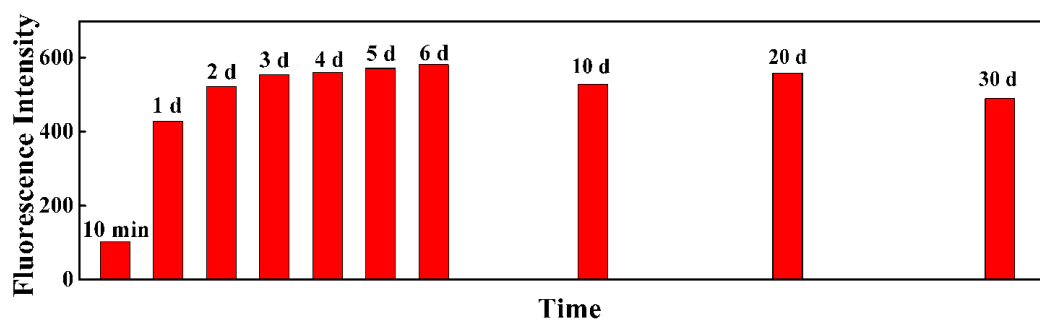
around

300

nm.

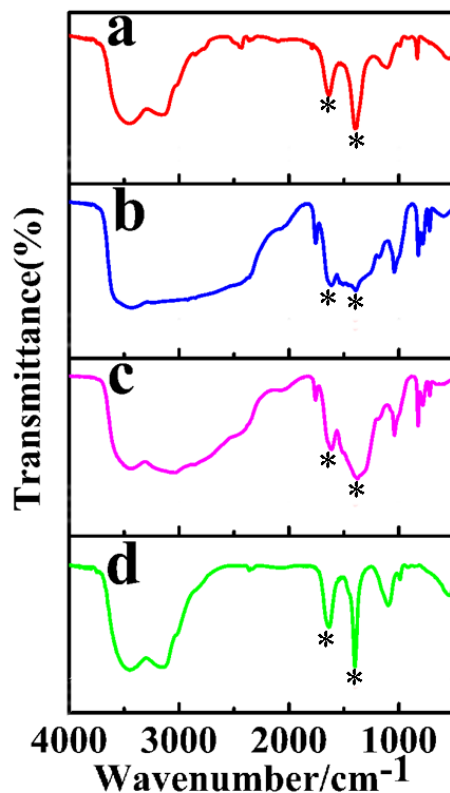


**Fig. S6** UV-vis absorption spectra of different concentrations of KNO<sub>3</sub> aqueous solutions. Inset is the plot of relationship of the KNO<sub>3</sub> concentration to absorbance.

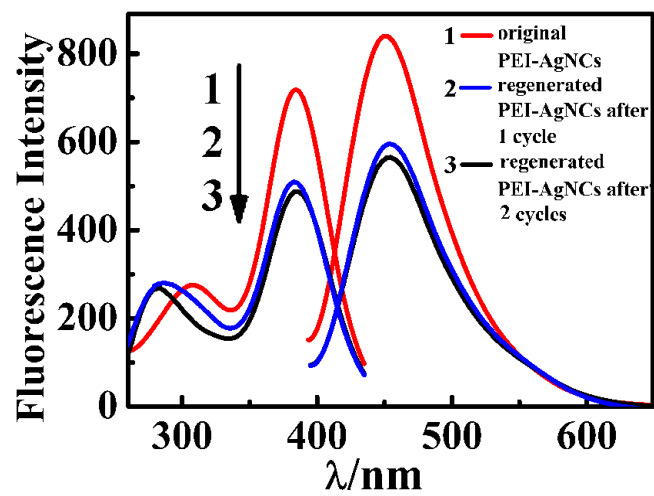


**Fig. S7** Change of fluorescence intensity of regenerated PEI-AgNCs at room temperature over time.





**Fig. S8** FT-IR spectra of original PEI-AgNCs (a), AgNPs (b), Ag(I) ions (c), and regenerated PEI-AgNCs (d). The original PEI-AgNCs showed two distinct peaks at 1635 and 1400 cm<sup>-1</sup>, which could be attributed to the formation of imine from the interaction between protonated primary amine and neighboring methylene after PEI reacted with AgNO<sub>3</sub>.<sup>S3,S4</sup> The two peaks shifted to 1612 and 1392 cm<sup>-1</sup> respectively when the small AgNCs agglomerated into AgNPs and further dissolved to Ag(I) ions, while the peaks at 1612 and 1392 cm<sup>-1</sup> shifted back to 1635 and 1400 cm<sup>-1</sup> again when PEI-AgNCs was regenerated.



**Fig. S9** Fluorescence spectra of original and regenerated PEI-AgNCs after 1 and 2 cycles, respectively.

## References

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