Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Nanosilver-enhanced AIE photosensitizer for simultaneous bioimaging and photodynamic therapy

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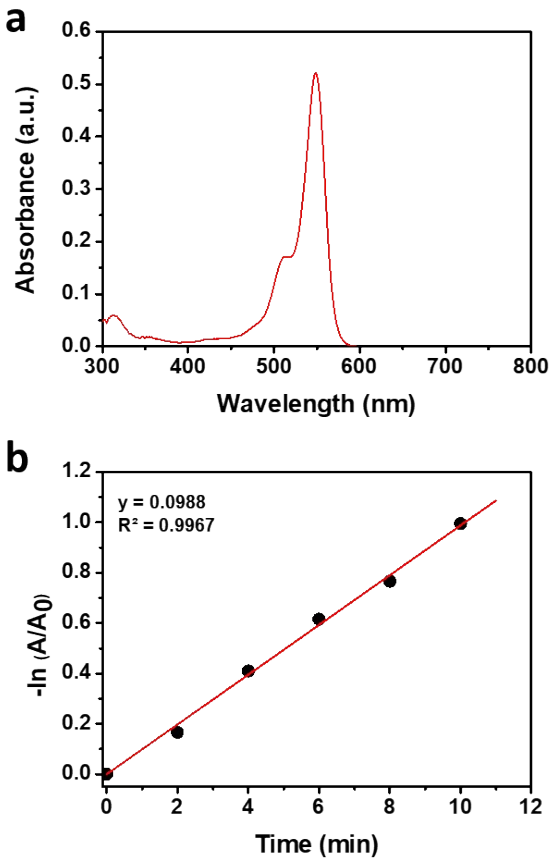

Figure S1. Absorbance spectra (a) and kinetic degradation of ABDA (50 µM) in the presence of Rose Bengal (5µM) in PBS solution and under continues 40 mW/cm^2 white light irradiation

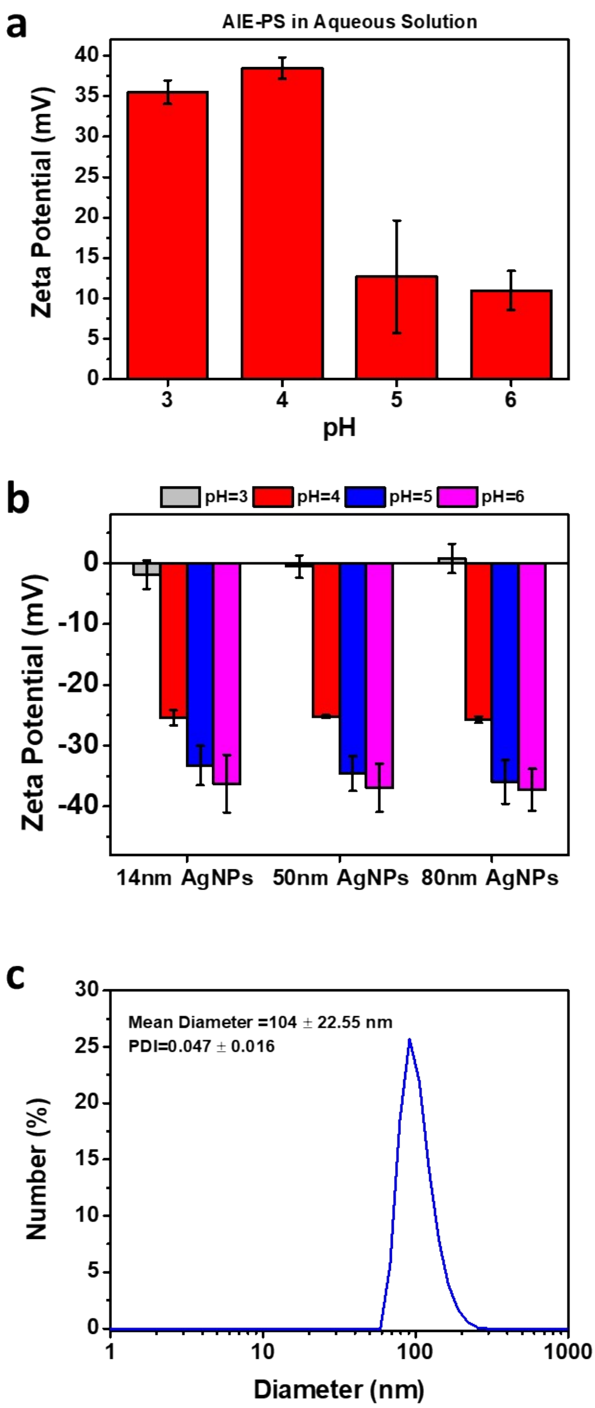

Figure S2. a) Zeta potential of AIE-PS solution at different pH, b) Zeta potential of 4-MBA capped AgNPs of different sizes (i.e., 14nm AgNPs , 50nm AgNPs and 80nm AgNPs) at different pH, c) Size distribution of the as-synthesized silica nanoparticles obtained by dynamic light scattering

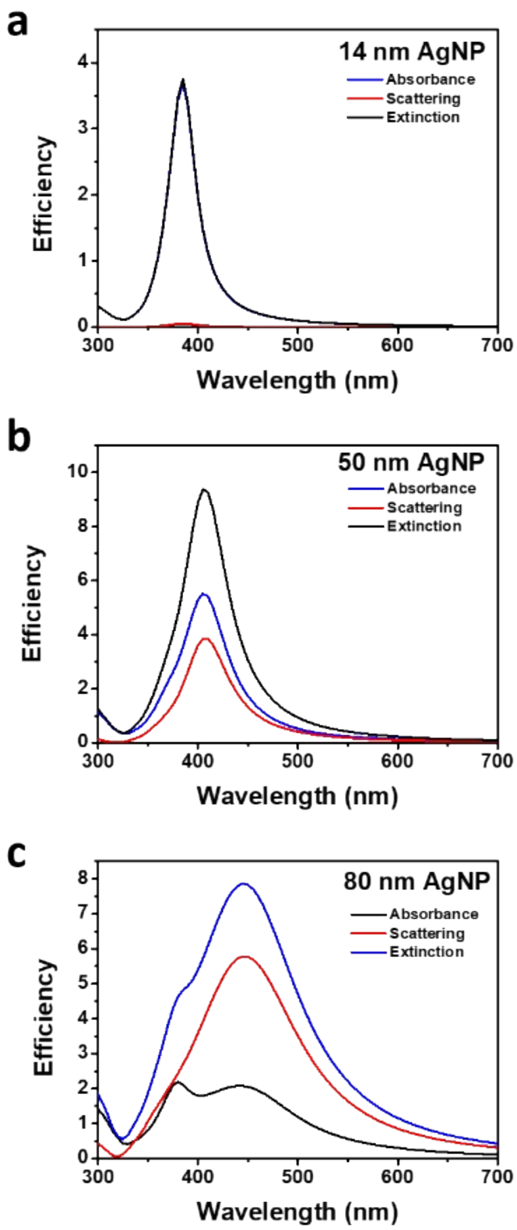

Figure S3. The simulated absorbance, light scattering and extinction spectra for a) 14 nm AgNP, b) 50 nm AgNP, and c) 80 nm AgNP, respectively.

SI-3 Stern-Volmer model:

The AgNPs quench the fluorescence intensity of AIE-PS, following the Stern-Volmer model as defined by the following expression:

$$\frac{F}{F_0} - 1 = K_{SV}[AgNPs] \qquad (S1)$$

where F and F_0 are maximum fluorescence intensity of AIE-PS in the presence and absence of varied AgNPs concentration ([AgNPs]). The Stern-Volmer quenching data for AIE-PS in the presence of a)14nm Ag NPs, b) 50nm Ag NPs, and c) 80nm Ag NPs can be found in **Figure S4**.

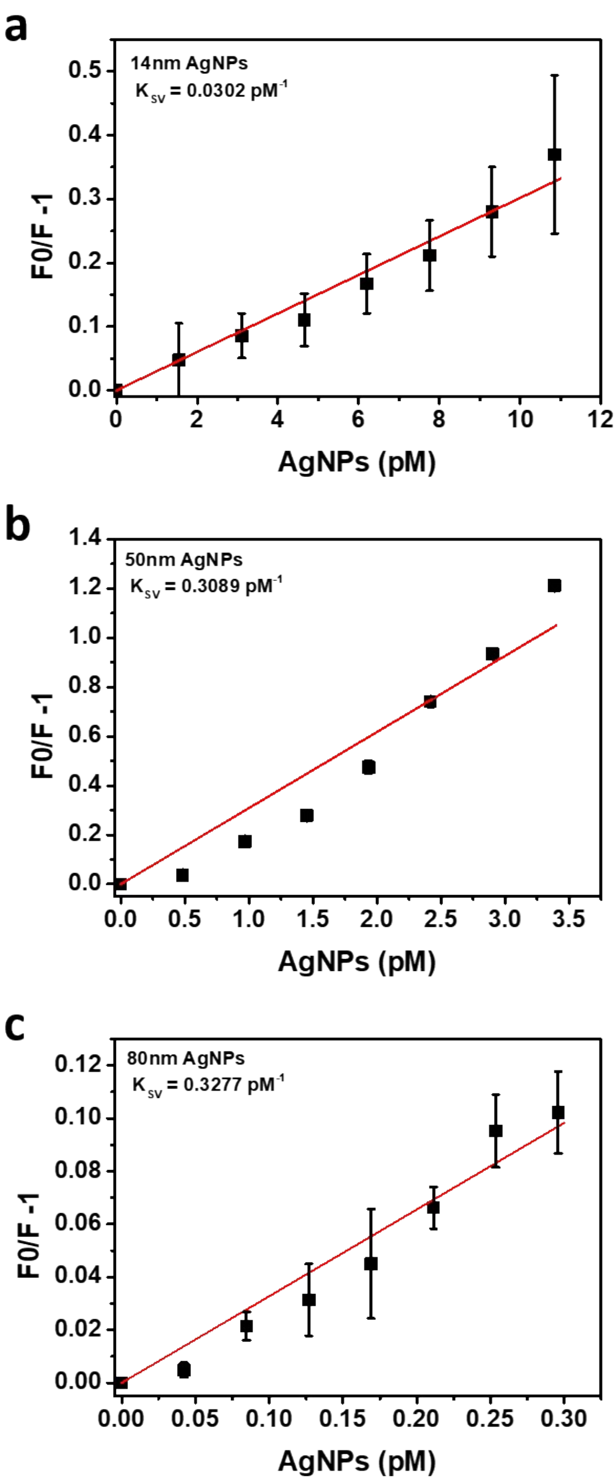

Figure S4. Stern-Volmer quenching data for AIE-PS in the presence of a) 14nm AgNPs, b) 50nm AgNPs, and c) 80nm Ag NPs

SI-5 Nanometal surface energy transfer (NSET) model:

In the NSET model, at a certain distance between the donor and acceptor (d_0), the possibility of energy transfer from excited dye molecules to the metallic surface becomes equal to the possibility of spontaneous emission from the dye. This distance (d_0) could be defined by the Persson-Lang surface energy equation as below [1]:

$$d_0 = \left(0.225 \frac{c^3 \varphi_{dye}}{\omega_{dye}^2 \omega_F k_F}\right)^{1/4} \quad (S2)$$

Where $\varphi_{dye}$and ω_F is fluorescence quantum yield and frequency of electronic transition of the dye, respectively. c is the speed of light, k_F and ω_F are Fermi wavevector and Fermi frequency of the metal, respectively. In this study, the fluorescence quantum yield data obtained for each hybrid sample (**Figure 4a**) was used as φ_{dye} in the above equation. ω_F was about 3.01×10^{15} s^{-1} based on the maximum emission wavelength of the AIE-dye (i.e., 625 nm). k_F and ω_F for AgNPs were as 1.2×10^{8} cm^{-1} and , 8.3×10^{15} s^{-1}, respectively [2, 3].

The energy transfer efficiency between the AIE-PS and AgNPs presented in **Figure 3c** was calculated according to the following formula, using the maximum fluorescence intensity of the AIE-PS in the presence (F) and absence (F_0) of AgNPs:

$$\varphi_{ET} = 1 - \frac{F}{F_0} \quad (S3)$$

Besides, the energy transfer efficiency is a function of the distance between the donor and acceptor using the following equation, where n = 4 for NSET model:

$$\varphi_{ET} = \frac{1}{1 + \left(\frac{R}{d_0}\right)^n} \quad (S4)$$

Hence, the dependencies of the eq. S3 and eq. S4 could be used to describe the experimental fluorescence quenching data obtained for AgNP@AIE-PS hybrid samples. By combining the two above formula and using the experimental results shown in **Figure 3a** and **Figure 3c**, the energy transfer efficiency could be fitted to the NSET model (**Figure 3d**).

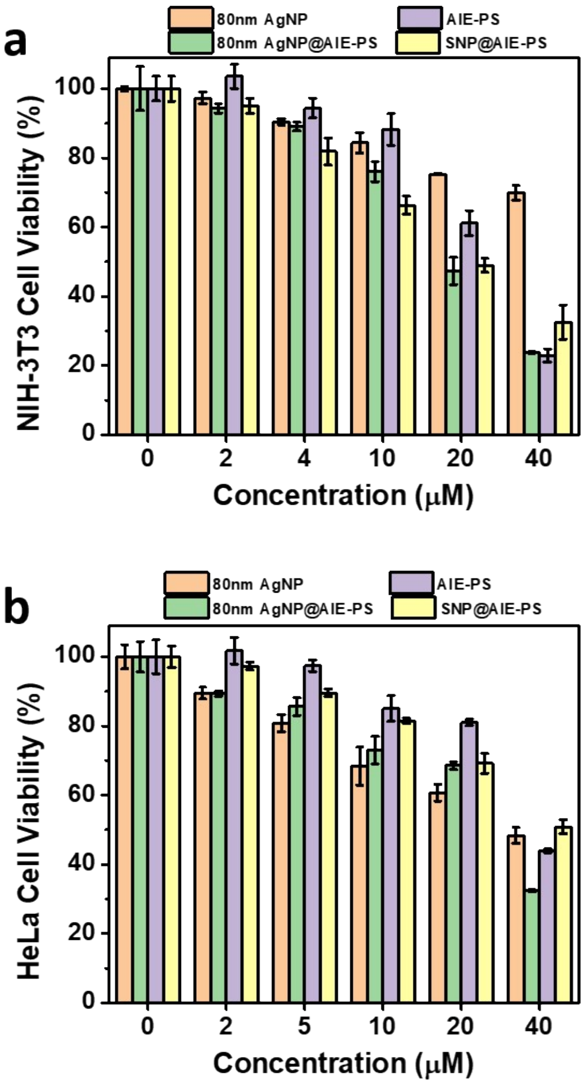

Figure S5. Metabolic viability of NIH-3T3 cells (a) and HeLa cells (b) as function of AIE-PS concentration (0-40 μM), after 24 hr incubation with 80nm AgNP@AIE-PS hybrid (green) , 9 μM AIE-PS alone (purple), SNP@AIE-PS (yellow), and 0.22 pM 80nm AgNPs alone (orange), respectively. For the hybrids, the concentration ratio of 80nm AgNPs (or silica nanoparticles) to AIE-PS was fixed at 0.22 pM/9 μM and 33.4 pM/9 μM, respectively.

REFERENCES

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3. R. Prajapati, A. Bhattacharya and T. K. Mukherjee, Resonant excitation energy transfer from carbon dots to different sized silver nanoparticles, *Phys. Chem. Chem. Phys.*, 2016, **18**, 28911-28918.