

## Supporting Information

### Metal-enhancement Study of Dual Functional Photosensitizers with Aggregation-Induced Emission and Singlet Oxygen Generation

Mohammad Tavakkoli Yaraki<sup>a,b,†</sup>, Fang Hu<sup>b,†</sup>, Soroosh Daqiqeh Rezaei<sup>a,c</sup>, Bin

Liu<sup>b,\*</sup>, Yen Nee Tan<sup>a,d,\*</sup>

<sup>a</sup> Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A\*STAR), 138634, Singapore

<sup>b</sup> Department Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117585, Singapore

<sup>c</sup> Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive 1, 117575, Singapore

<sup>d</sup> Faculty of Science, Agriculture & Engineering, Newcastle University, Newcastle Upon Tyne NE1 7RU, United Kingdom

<sup>†</sup>M. Tavakkoli Yaraki and F. Hu contributed equally to this work.

#### \*Corresponding Authors

**Prof. Yen Nee Tan** (Email: [yennee.tan@ncl.ac.uk](mailto:yennee.tan@ncl.ac.uk))

**Prof. Bin Liu** (Email: [cheliub@nus.edu.sg](mailto:cheliub@nus.edu.sg))

## Experimental Section

### Materials

Poly(ethyleneimine) solution (PEI, 50%, Mw=2000), poly(sodium 4-styrene sulfonate) (PSS, Mw=70000), tannic acid, nitric acid, hydrochloric acid, potassium carbonate, silver nitrate, 9,10-anthracenediyl-bis(methylene)dimalonic acid (ABDA), Tetraethyl orthosilicate (TEOS), ethanol, ammonia solution, and sodium chloride were purchased from Sigma-Aldrich, Germany. For the synthesis of AIEgens, chemicals were all purchased from Sigma-Aldrich and used as received without further purification. Tetrahydrofuran (THF) and dichloromethane were dried by distillation using sodium or calcium hydride as the drying agent. All non-aqueous reactions were carried out under the nitrogen atmosphere in oven-dried glassware. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc.

### Characterization

The extinction of AgNPs and the absorbance of ABDA was measured by a UV-Vis spectrophotometer (Shimadzu, UV-1700, Japan). The fluorescence of the samples was obtained using Infinite M-200 Microplate reader. Transmission electron microscopy (TEM) images were taken by JEOL JEM-2010F operating at 200kV. The zeta potential and hydrodynamic size of the nanoparticles were acquired on Malvern Zetasizer at room temperature. Fluorescence lifetime was measured using a FluoTime 200 TCSPC machine (Picoquant BmbH, Germany). Nuclear magnetic resonance (NMR) spectra were measured on a Bruker ARX 400 NMR spectrometer. Chemical shifts are reported in parts per million referenced with respect to residual solvent ( $\text{CDCl}_3 = 7.26$  ppm, MeOD = 3.31 ppm) for  $^1\text{H}$  NMR and ( $\text{CDCl}_3 = 77.1$  ppm, MeOD = 49.0) for  $^{13}\text{C}$  NMR. The extent of reaction was monitored by thin-layer chromatography (TLC) using Merck 60 F254 pre-coated silica gel plates with fluorescent indicator UV254 after the plates were subjected to elution in the TLC chamber. Flash column chromatography was carried out using Merck silica gel (0.040-0.063).

### **Synthesis of AIEgens**

Compound 1,<sup>1</sup> compound 2,<sup>2</sup> and AIE-R-SOG<sup>3</sup> were synthesized according to the reported literature.

**AIE-B:** Trimethylamine (2 mL, 25 wt. % in H<sub>2</sub>O) was added dropwise into compound 1 (100 mg, 0.21 mmol) in methanol (20 mL) under 20 °C. After stirring at 20 °C overnight, the solvent and excess trimethylamine were removed under reduced pressure. The obtained residue was dissolved in water (20 mL) and washed by dichloromethane (50mL × 3). The aqueous phase was dried by freeze drier to obtain AIE-B as white powder (85 mg, yield 76.2%). <sup>1</sup>H NMR (400 MHz, MeOD) δ 7.13–7.05 (m, 9H), 7.04–6.97 (m, 6H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 4.00 (t, *J* = 5.9 Hz, 2H), 3.48–3.42 (m, 2H), 3.17 (s, 9H), 2.05–1.94 (m, 2H), 1.85 (dd, *J* = 13.5, 6.1 Hz, 2H). <sup>13</sup>C NMR (101 MHz, MeOD) δ 157.47, 143.96, 140.60, 140.26, 136.24, 132.21, 130.96, 127.34, 126.03, 113.35, 66.49, 66.17, 52.20, 25.75, 19.72. The purity of the sample was about 99%.

**AIE-Y-SOG:** Compound 2 (78 mg, 0.18 mmol) and bromoethane (110 mg, 1.1 mmol) were dissolved in DMF (5 mL) and heated at 80 °C under argon atmosphere for 14 h. After cooling to room temperature, the mixture was separated with chromatography directly (Eluent: hexane/ethyl acetate = 1/5, dichloromethane/methanol = 10/1) to get the desired product as a yellow solid (80 mg, yield 81.1 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.12 (d, *J* = 6.3 Hz, 2H), 7.93 (d, *J* = 6.3 Hz, 2H), 7.56 (d, *J* = 16.2 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.07 – 7.01 (m, 10H), 6.95 (dd, *J* = 5.6, 2.4 Hz, 8H), 4.79 (q, *J* = 7.2 Hz, 2H), 1.60 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.52, 147.17, 144.02, 143.30, 143.24, 143.11, 142.52, 141.94, 139.97, 132.43, 132.17, 131.28, 127.91, 127.88, 127.70, 126.94, 126.86, 124.11, 121.68, 56.24, 17.01. The purity of the sample was about 95%.

### ***Synthesis of silver nanoparticles (AgNPs)***

Aqua regia (HCl: HNO<sub>3</sub> with 3:1 molar ratio) was used to wash all glassware before the synthesis. Then, glassware was washed with DI-water and ethanol and, finally, with D-water.

The silver nanoparticles (AgNPs) with different sizes were synthesized using tannic acid as both reducing agent and capping agent according to the literature<sup>4</sup>. Briefly, the 19.5 mL of tannic acid solution was prepared freshly, and the pH was adjusted to the desired value using K<sub>2</sub>CO<sub>3</sub> solution (0.5 M or 0.05 M). Then, 500 μL of AgNO<sub>3</sub> solution (20×10<sup>-3</sup> M) was added to the above reaction. For 25 nm and 40 nm AgNPs, the Ag/TA molar ratio was kept at 5, and the pH was adjusted at 7 and 6, respectively. For 85 nm AgNPs, the Ag/TA molar ratio increased to 20, and the pH was adjusted at 6. All synthesis experiments were carried out at 30 °C.

### ***Self-assembly of polyelectrolytes on AgNPs***

The polyelectrolyte coating of AgNPs was performed using layer-by-layer (LBL) approach<sup>5</sup>. The PEI and PSS solutions (both 10 mM based on Mw of repeat unit) were prepared using NaCl solution (10 ×10<sup>-3</sup> M) as the solvent, and then the pH was changed to 3 using HCl solution (1M). A washing solution also was prepared using 10 mM NaCl solution and HCl (1 M) with a pH of 3. In addition to the NaCl concentration which reduces the electrostatic repulsion, it has been reported that the thickness of polyelectrolytes on the substrate is a function of the deposition pH. Selection of these parameters is important to obtain a thin layer of PEI/PSS bilayer and enables linear growth of thickness for each bilayer.<sup>6-8</sup> In LBL approach, the degree of aggregation could be controlled by performing the LBL at a low concentration of AgNPs and also sonication of samples during the assembly process. For LBL, AgNPs solution (250 μL) was added to PEI solution (750 μL), vortexed for 30 sec and sonicated for 10 min. After 3 times washing, the same procedure was done with PSS solution. The AgNPs with different bilayers of PEI/PSS were prepared by repeating the previous steps.

### ***Synthesis of silica nanoparticles***

Silica nanoparticles (~100 nm) were synthesized according to the modified Stöber method reported in our previous work<sup>9,10</sup>.

### ***Metal-enhanced fluorescence study***

To study the MEF, the same amount of fluorophore should exist in all samples. Hence, an adequate amount of AIEgen solution ( $0.15 \times 10^{-3}$  M) was added to polymer-coated AgNPs and sonicated for 15 min. Then, the sample was centrifuged, and the supernatant was removed, and the precipitate was diluted with PBS to reach 1 mL volume. By comparing the absorbance of the supernatant and control sample without AgNPs, the amount of AIEgen in all samples was kept constant at a concentration of  $10 \times 10^{-6}$  M. The control samples for MEF also were prepared with the same amount of AIEgen (AIE-Y-SOG and AIE-R-SOG, and AIE-B) loaded on silica nanoparticle. For the fluorescence study, 40  $\mu$ L of each solution was transferred to a 394-well black microplate.

### ***Singlet oxygen generation measurement***

ABDA was used as an indicator of singlet oxygen generation. A 1 mL solution containing  $10 \times 10^{-6}$  M AIE photosensitizer (AIE-PS) adsorbed on polymer-coated AgNPs and 50  $\mu$ M ABDA was prepared and exposed to the 40 mWcm<sup>-2</sup> white light. The degradation of ABDA was monitored by measuring the UV-Vis absorbance spectra of ABDA. The first-order kinetic model ( $-\ln\left(\frac{A}{A_0}\right) = kt$ ) was used to determine the degradation rate of ABDA and consequently, the singlet oxygen generation rate of AIE-PS enhanced by the AgNPs in the nanohybrids.<sup>11</sup> The loaded AIE-PS molecules on silica nanoparticles (SiNP) were used as a control.

The enhancement in singlet oxygen generation was calculated based on the below equation:

$$\text{Singlet oxygen generation enhancement factor } (EF_{SOG}) = \frac{k_{Ag@AIE}}{k_{Si@AIE}} \quad \text{eq. (S1)}$$

where  $k_{Ag@AIE}$  is the first-order kinetic constant for degradation of ABDA in the presence of AIE-PS on AgNPs with different bilayers of polyelectrolytes and the  $k_{Si@AIE}$  is the same parameter for the control sample, which is aggregated AIE-PS on silica nanoparticles.

### Fluorescence Lifetime measurement

2 mL of each sample containing  $10 \times 10^{-6}$  M AIEgen was diluted to 3 mL using DI-water, and the fluorescence lifetime was measured by excitation at 374 nm for AIE-Y-SOG samples, 374 nm for AIE-R-SOG samples and 321 nm for AIE-B samples. The emission wavelength was set according to the maximum fluorescence of each AIEgen. The biexponential model was used to describe the fluorescence decay which can be defined as below:

$$I(t) = \sum \alpha_i \exp(-t/\tau_i) \quad \text{eq.} \quad (S2)$$

Where  $\tau_i$  is decay time,  $\alpha_i$  is amplitude, and  $\sum \alpha_i = 1$ .

The amplitude-weighted fluorescence lifetime is defined as:

$$\langle \tau \rangle = \sum \alpha_i \tau_i \quad \text{eq.} \quad (S3)$$

Moreover, the average lifetime can be written as:

$$\bar{\tau} = \sum f_i \tau_i \quad \text{eq.} \quad (S4)$$

$$f_i = \frac{\alpha_i \tau_i}{\sum \alpha_i \tau_i}$$

Where the contribution fraction of each component is given as follows:

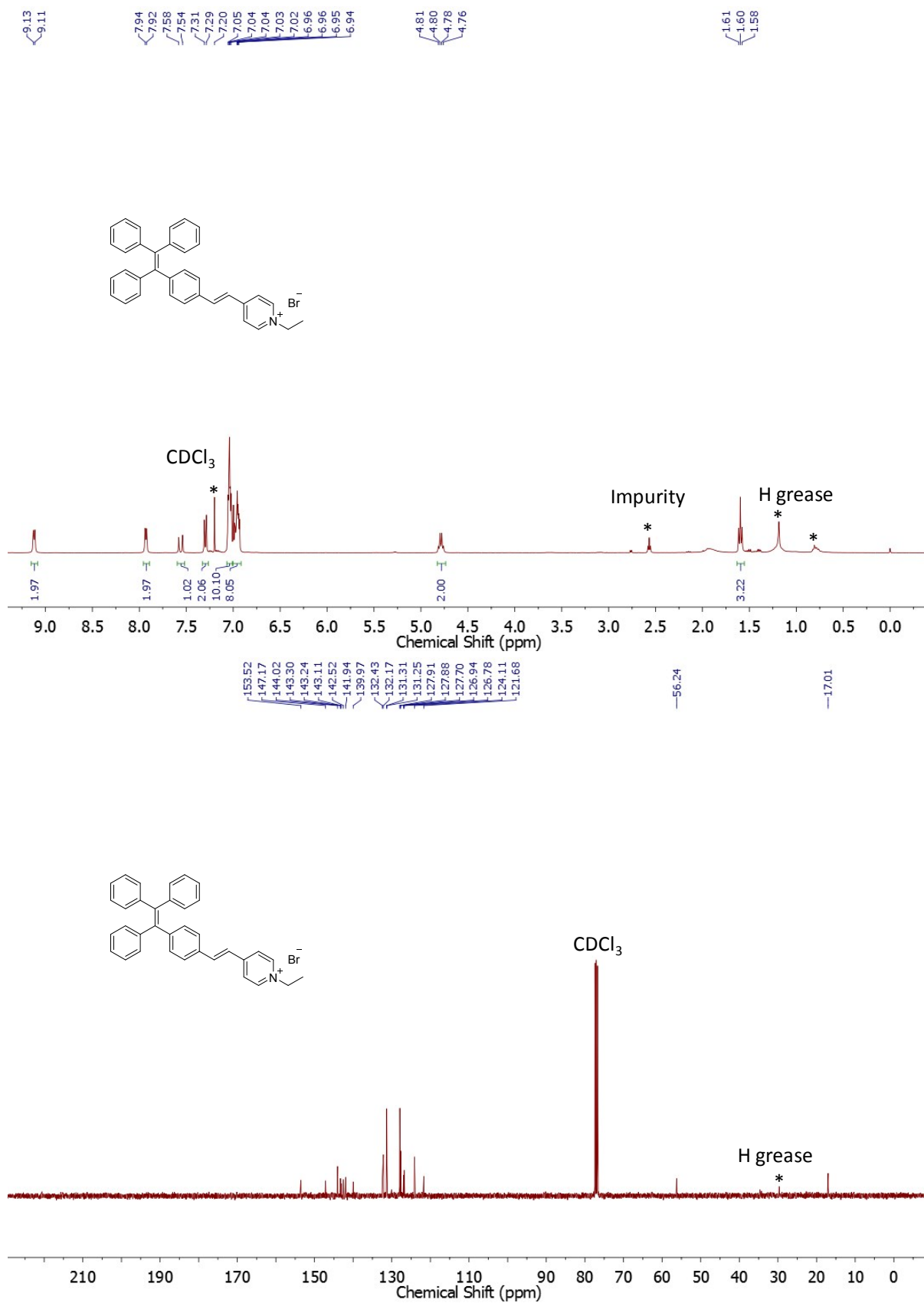
eq. (S5)

The curve fitting was performed using the Curve-fitting toolbox in Matlab2014b software.

### ***Simulation of the electric field distribution***

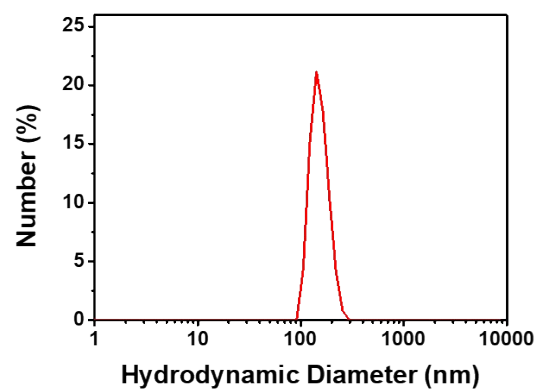
To simulate the enhanced electric field around the silver nanoparticles, Finite element method (FEM) based simulations were carried out by the COMSOL Multiphysics software package (see [www.comsol.com](http://www.comsol.com)). The complex refractive index of Ag was taken from CRC handbook<sup>12</sup>. Water was used as the surrounding environment. A plane wave propagating in the y-direction and linearly polarized along the z-axis spanning the wavelength range of 300 nm to 700 nm was set as the source. Due to the symmetry of the problem only one-quarter of the sphere was modeled. To ensure high accuracy, the mesh size for all simulations was chosen as 0.5 nm. To calculate the electric field distribution a total field scattered field (TFSF) analysis was used.

In order to calculate the average surface electric field, individual Ag nanoparticles ( $d = 25, 40, 85$  nm) were illuminated by a plane wave at 385 nm. The real part of the electric field was integrated over the volume of the spherical shell surrounding the nanoparticle and on the outer surface of the shell. The results were divided by the spherical shell outer surface area, respectively, to generate the average surface electric field.

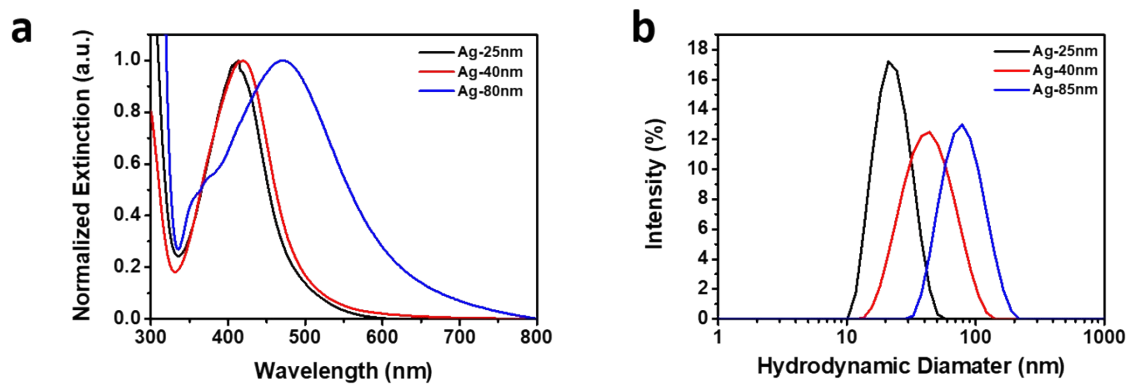


**Figure S1.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of AIE-Y-SOG in CDCl<sub>3</sub>.

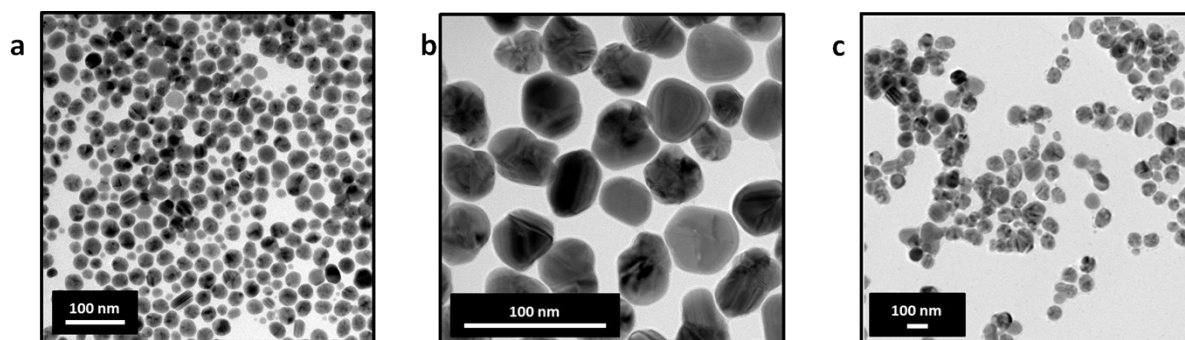




**Figure S2.** The hydrodynamic size distribution of AIE-Y-SOG in PBS:DMSO (99:1) as measured by the dynamic light scattering (DLS) instrument



**Figure S3.** a) Extinction spectra and b) DLS data of AgNPs of different sizes (25, 40, and 85 nm)



**Figure S4.** TEM images of AgNPs of different sizes: a) 25 nm, b) 40 nm, and c) 85 nm

---

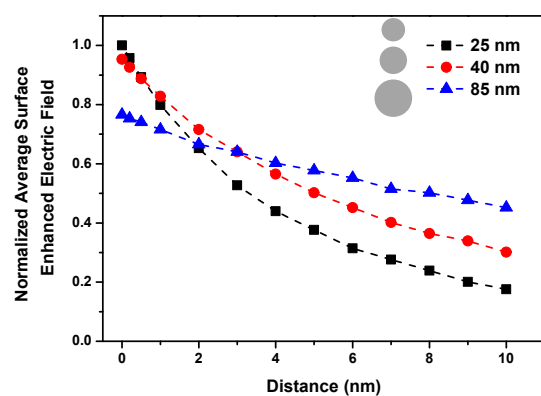
**Table S1- Fluorescence lifetime analysis for AIE-Y-SOG in different mediums and**

---

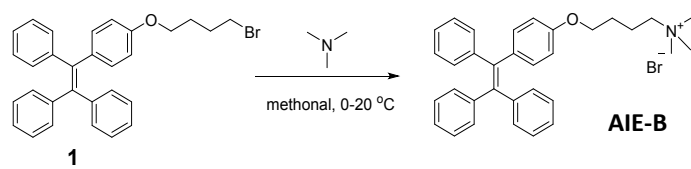
**Ag@AIE-Y-SOG prepared using different size of AgNPs and different number of PEI/PSS bilayers**

<b>Sample</b>	<b><math>\alpha_i</math></b>	<b><math>\tau_i(\text{ns})</math></b>	<b><math>f_i</math></b>	<b><math>\bar{\tau}(\text{ns})</math></b>	<b><math>\langle\tau\rangle(\text{ns})</math></b>
AIE-Y-SOG in Water	0.501	3.433	0.32324	5.984	5.316
	0.499	7.202	0.67676		
Si@AIE-Y-SOG	0.803	1.596	0.5246	3.639	2.443
	0.197	5.893	0.4654		
25Ag/1BL@AIE-Y-SOG	0.573	1.183	0.226963	4.449	2.987
	0.427	5.407	0.773037		
25Ag/2BL@AIE-Y-SOG	0.546	1.739	0.253108	5.044	3.750
	0.454	6.164	0.746892		
25Ag/3BL@AIE-Y-SOG	0.639	2.007	0.345701	5.090	3.709
	0.361	6.718	0.654299		
40Ag/1BL@AIE-Y-SOG	0.568	1.359	0.236838	4.712	3.258
	0.432	5.753	0.763162		
40Ag/2BL@AIE-Y-SOG	0.680	2.677	0.409942	5.920	4.438
	0.320	8.173	0.590058		
40Ag/3BL@AIE-Y-SOG	0.516	1.905	0.231109	5.642	4.256
	0.484	6.765	0.768891		
85Ag/1BL@AIE-Y-SOG	0.498	1.754	0.207285	5.634	4.212
	0.502	6.649	0.792715		
85Ag/2BL@AIE-Y-SOG	0.507	6.6	0.792222	5.599	4.227
	0.493	1.783	0.207778		
85Ag/3BL@AIE-Y-SOG	0.526	1.955	0.242386	5.611	4.243
	0.474	6.781	0.757614		

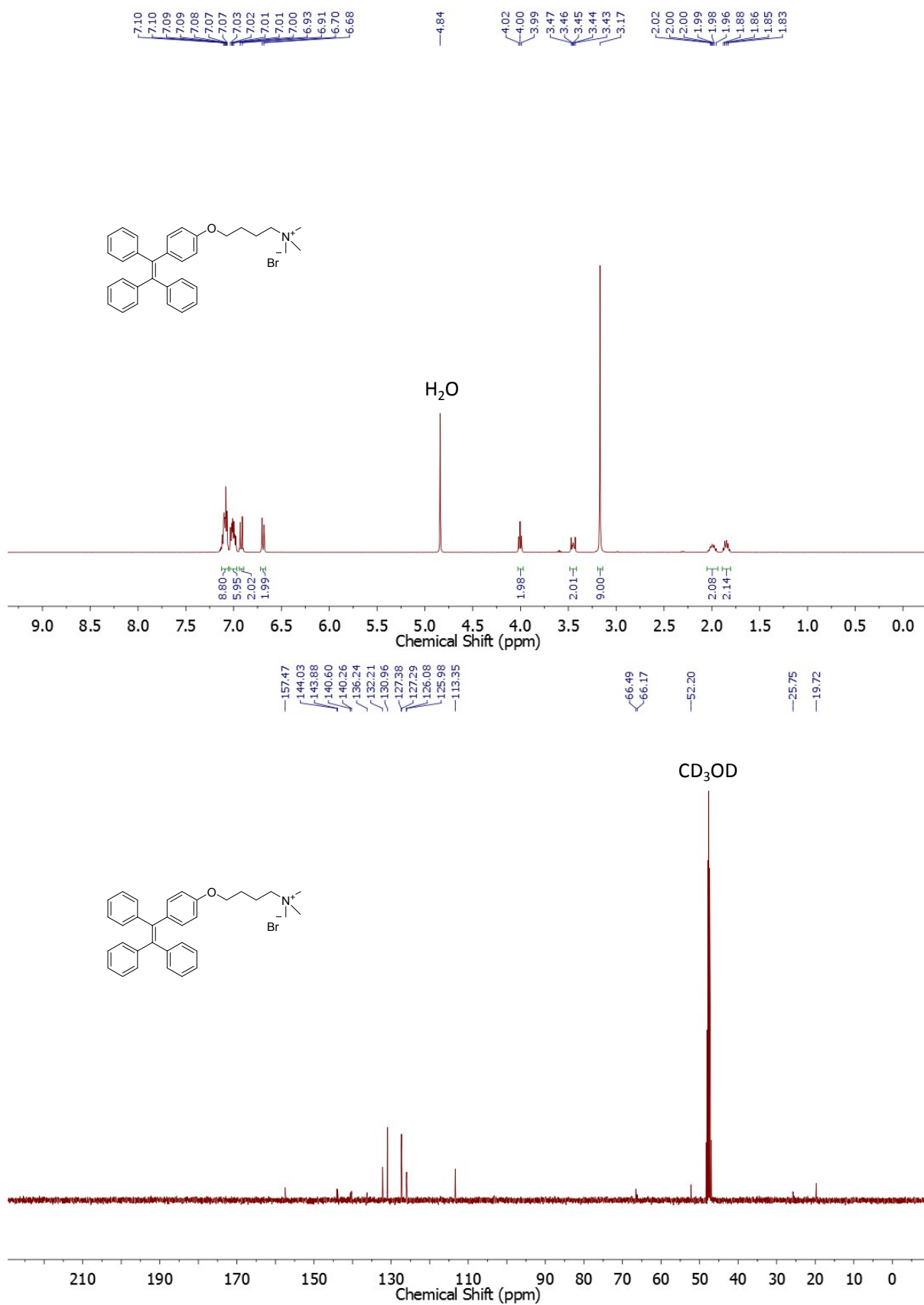
$\bar{\tau}$  :Average lifetime  
 $\langle\tau\rangle$ :Amplitude – weighted lifetime



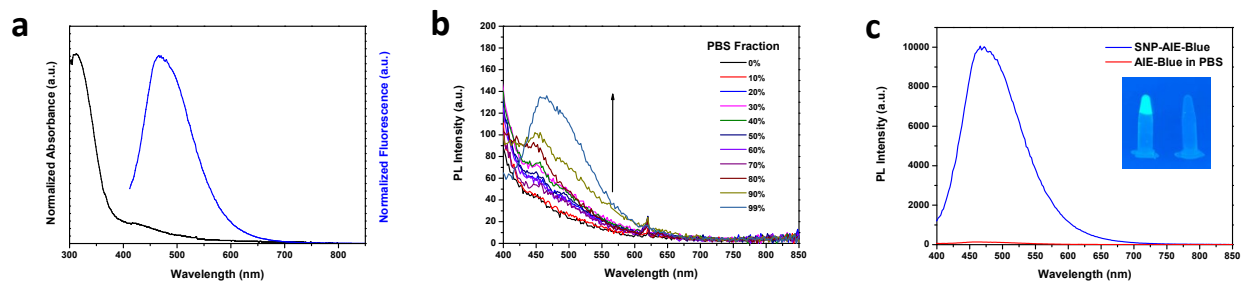
**Figure S5.** Normalized surface average enhanced electric field around AgNPs with different size as a function of distance from the surface of the nanoparticle



**Scheme S1.** Synthetic route of AIE-B

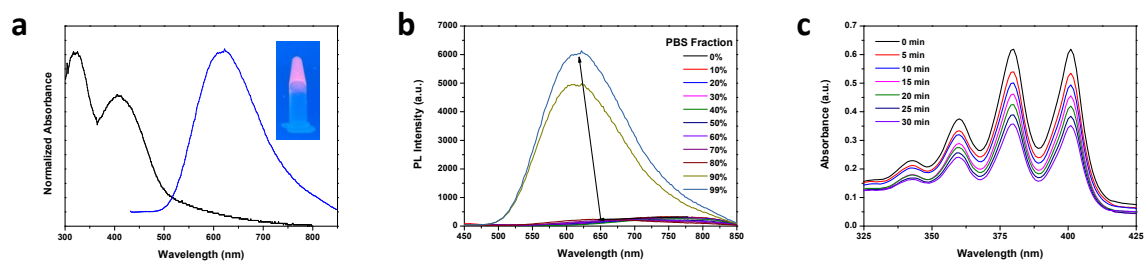


**Figure S6.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of AIE-B in CD<sub>3</sub>OD.



**Figure S7.** a) Absorbance and fluorescence spectra of AIE-B, b) Effect of PBS fraction on fluorescence spectra of AIE-B, c) Fluorescence spectra of AIE-B in PBS solution and loaded on silica NPs. The insets show the optical photographs of these samples obtained under 365 nm light irradiation





**Figure S8.** a) Absorbance and fluorescence spectra of AIE-R-SOG in PBS, Inset shows optical photograph obtained under 365 nm light irradiation b) Effect of PBS fraction on fluorescence spectra of AIE-R-SOG, c) Degradation of 50  $\mu\text{M}$  ABDA in the presence of 10  $\mu\text{M}$  AIE-R-SOG in PBS under 40  $\text{mWcm}^{-2}$  white light

---

**Table S2- Fluorescence lifetime analysis for AIE-B in different mediums**

---

and Ag@AIE-B prepared using different size of AgNPs and different number of PEI/PSS bilayers

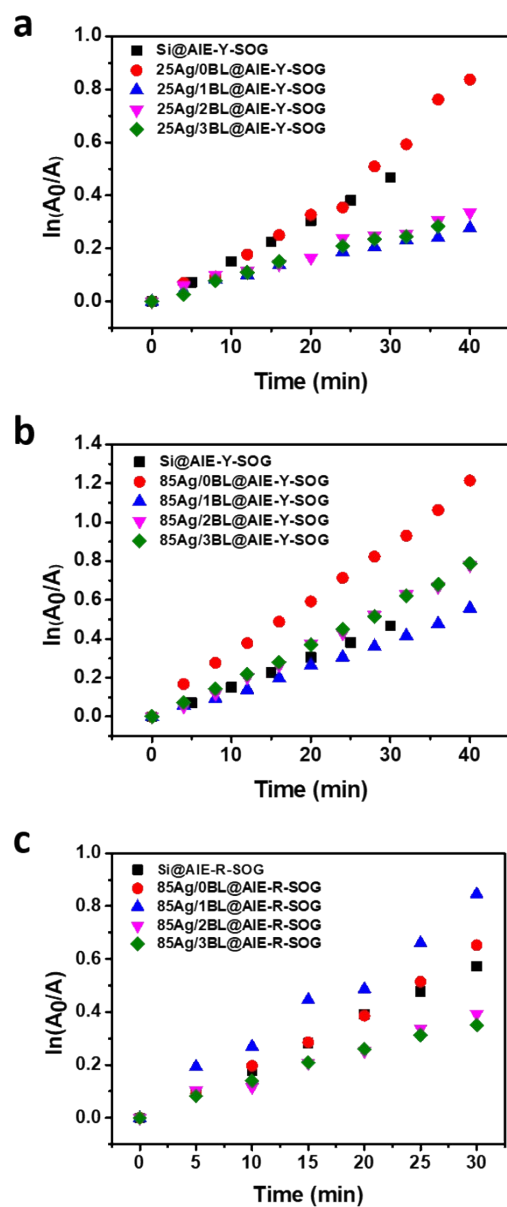
Sample	$\alpha_i$	$\tau_i(\text{ns})$	$f_i$	$\bar{\tau}(\text{ns})$	$\langle\tau\rangle(\text{ns})$
AIE-B in Water	0.8839	0.81	0.36627	7.059	1.954
	0.1161	10.67	0.63373		
Si@AIE-B	0.9244	1.494	0.70817	3.255	1.950
	0.0756	7.528	0.29183		
85Ag/1BL@AIE-B	0.9662	1.516	0.76930	4.161	1.904
	0.0338	12.98	0.23070		
85Ag/2BL@AIE-B	0.9107	1.486	0.68009	3.290	1.990
	0.0893	7.126	0.31991		
85Ag/3BL@AIE-B	0.9534	1.831	0.77710	3.822	2.247
	0.0466	10.76	0.22290		

$\bar{\tau}$ : Average lifetime  
 $\langle\tau\rangle$ : Amplitude – weighted lifetime

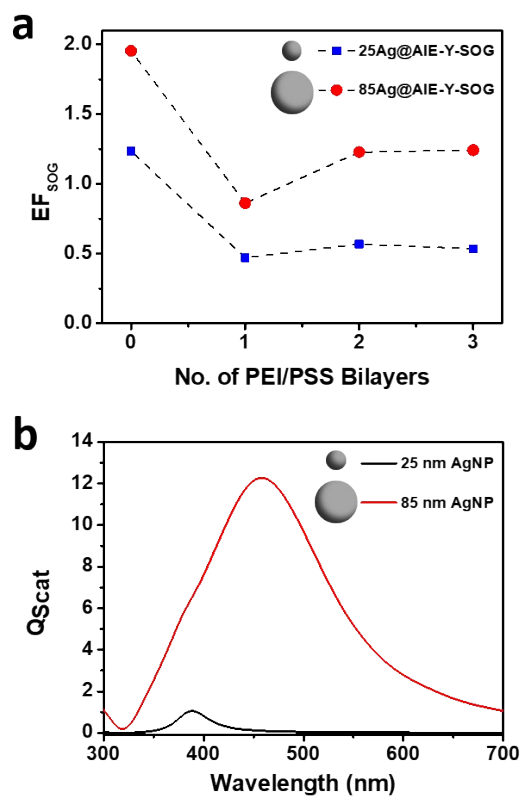
**Table S3- Fluorescence lifetime analysis for AIE-R-SOG in different mediums and Ag@AIE-R-SOG prepared using different size of AgNPs and different number of PEI/PSS bilayers**

<b>Sample</b>	$\alpha_i$	$\tau_i(\text{ns})$	$f_i$	$\bar{\tau}(\text{ns})$	$\langle\tau\rangle(\text{ns})$
AIE-R-SOG in Water	0.3897	2.078	0.2642	3.269	3.065
	0.6103	3.696	0.7358		
Si@AIE-R-SOG	0.0686	0.811	0.7161	1.821	1.055
	0.9314	4.369	0.2839		
85Ag/1BL@AIE-R-SOG	0.8991	0.6313	0.60414	1.841	0.936
	0.1009	3.686	0.39586		
85Ag/2BL@AIE-R-SOG	0.90567	0.5807	0.60122	1.824	0.875
	0.09433	3.698	0.39878		
85Ag/3BL@AIE-R-SOG	0.8356	0.7139	0.51914	1.987	1.149
	0.1644	3.361	0.48086		

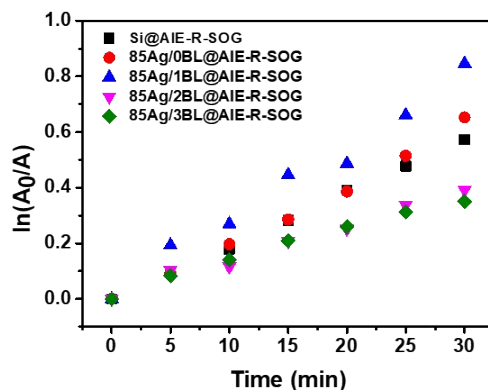
$\bar{\tau}$  :Average lifetime  
 $\langle\tau\rangle$ :Amplitude – weighted lifetime



**Figure S9.** Degradation of 50  $\mu\text{M}$  ABDA in the presence of  $10 \times 10^{-6}$  M AIEgen loaded on AgNPs with different PEI/PSS bilayers and under  $40 \text{ mWcm}^{-2}$  white light a) 25 nm Ag@AIE-Y-SOG, b) 85 nm Ag@AIE-Y-SOG, c) 85 nm Ag@AIE-R-SOG



**Figure S10.** a) Metal-enhanced singlet oxygen generation of 25 nm (square) and 85 nm (sphere) Ag@AIE-Y-SOG nano hybrids with different PEI/PSS bilayers, b) Simulated scattering efficiency spectra for 25 nm and 85 nm AgNP placed in water as a medium



**Figure S11.** Degradation of 50  $\mu\text{M}$  ABDA in the presence of  $10 \times 10^{-6}$  M AIE-R-SOG loaded on 85 nm AgNPs with different PEI/PSS bilayers and under  $40 \text{ mWcm}^{-2}$  white light.

## References

1. X. Xu, W. Lv, J. Huang, J. Li, R. Tang, J. Yan, Q. Yang, J. Qin and Z. Li, *RSC Advances*, 2012, **2**, 7042-7047.
2. X. Chen, X. Y. Shen, E. Guan, Y. Liu, A. Qin, J. Z. Sun and B. Z. Tang, *Chemical Communications*, 2013, **49**, 1503-1505.
3. F. Hu, X. Cai, P. N. Manghnani, W. Wu and B. Liu, *Chem. Sci.*, 2018, **9**, 2756-2761.
4. Y. Cao, R. Zheng, X. Ji, H. Liu, R. Xie and W. Yang, *Langmuir*, 2014, **30**, 3876-3882.
5. A. Elbakry, E. C. Wurster, A. Zaky, R. Liebl, E. Schindler, P. Bauer - Kreisel, T. Blunk, R. Rachel, A. Goepferich and M. Breunig, *Small*, 2012, **8**, 3847-3856.
6. J. Liang, K. Li, G. G. Gurzadyan, X. Lu and B. Liu, *Langmuir*, 2012, **28**, 11302-11309.
7. C. Jiang, X. Liu, C. Luo, Y. Zhang, L. Shao and F. Shi, *J. Mat. Chem. A*, 2014, **2**, 14048-14053.
8. C. Tedeschi, L. Li, H. Möhwald, C. Spitz, D. von Seggern, R. Menzel and S. Kirstein, *Journal of the American Chemical Society*, 2004, **126**, 3218-3227.
9. W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62-69.
10. Y. Wang and B. Liu, *Langmuir*, 2009, **25**, 12787-12793.
11. N. A. Kuznetsova, N. S. Gretsova, O. A. Yuzhakova, V. M. Negrimovskii, O. L. Kaliya and E. A. Luk'yanets, *Russ. J. Gen. Chem.*, 2001, **71**, 36-41.
12. J. F. Shackelford, Y.-H. Han, S. Kim and S.-H. Kwon, *CRC materials science and engineering handbook*, CRC press, 2016.