

# Supporting Information

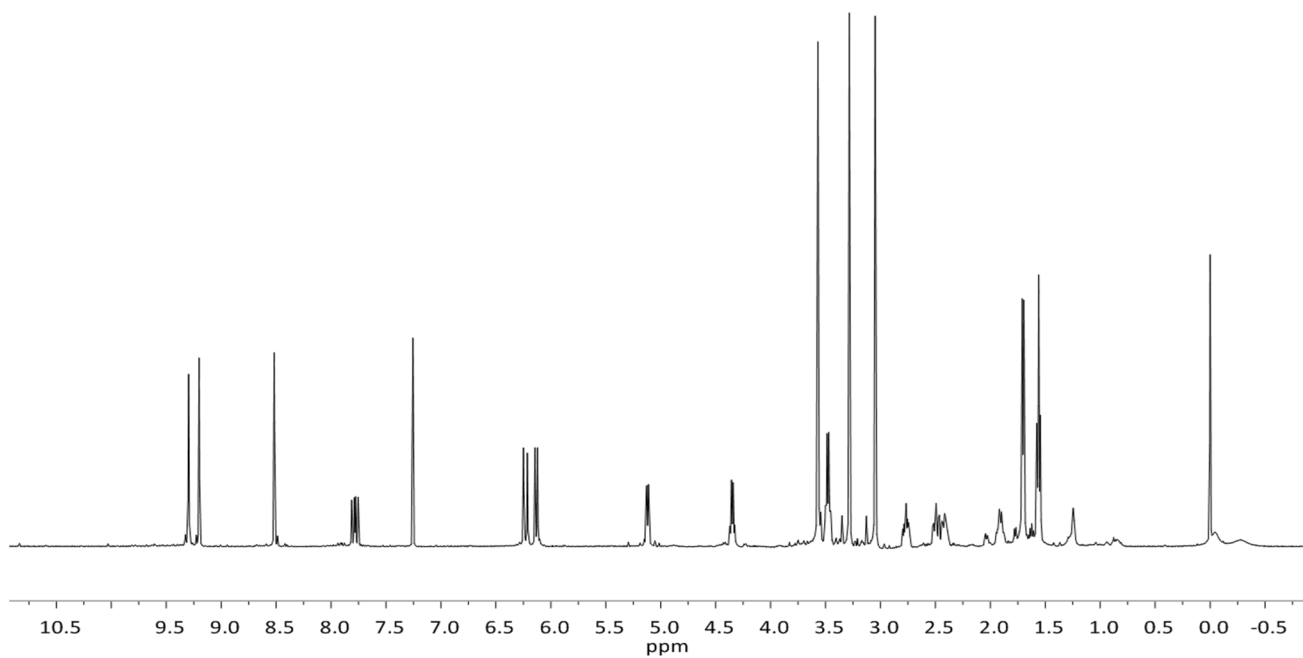
Graphene Oxide Nanoparticles Having Long Wavelength  
Absorbing Chlorins for Highly Enhanced Photodynamic  
Therapy with Reduced Dark Toxicity

Eun Seon Kang,<sup>[a]</sup> Tae Heon Lee,<sup>[a]</sup> Yang Liu,<sup>[a]</sup> Ki-Ho Han,<sup>[a]</sup> Woo Kyoung Lee,<sup>\*[a]</sup> and Il  
Yoon<sup>\*[a]</sup>

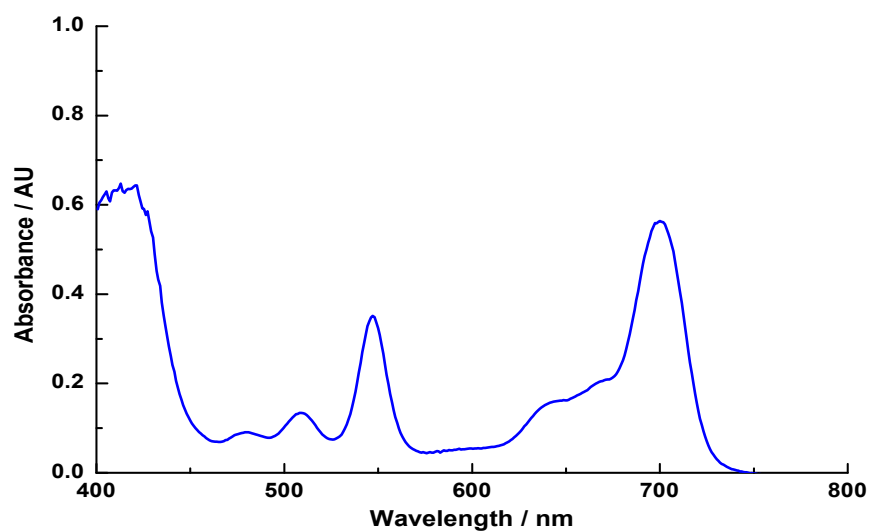
Center for Nano Manufacturing and Department of Nanoscience and Engineering,  
Inje University, 197 Injero, Gimhae, Gyeongnam 50834, Republic of Korea

\*E-mail : yoonil71@inje.ac.kr (I. Y.); wlee@inje.ac.kr (W. K. L.)

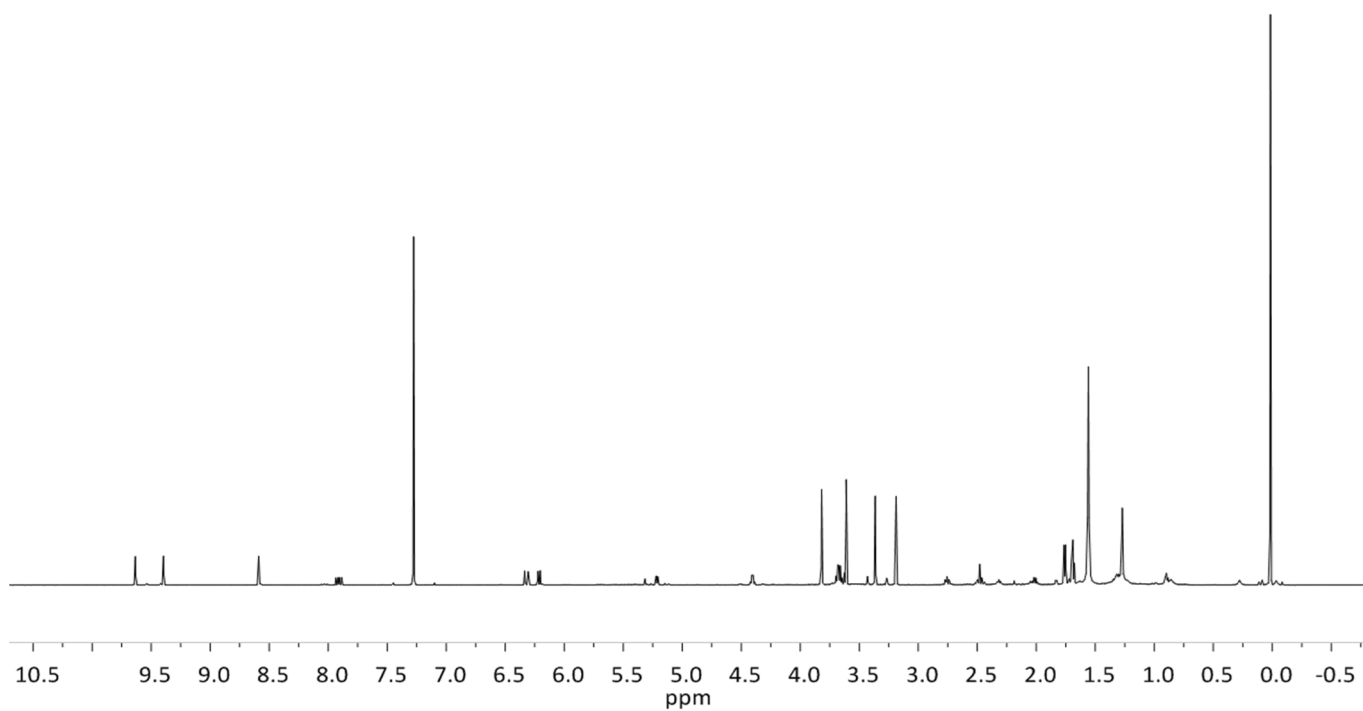
## Characterization Data



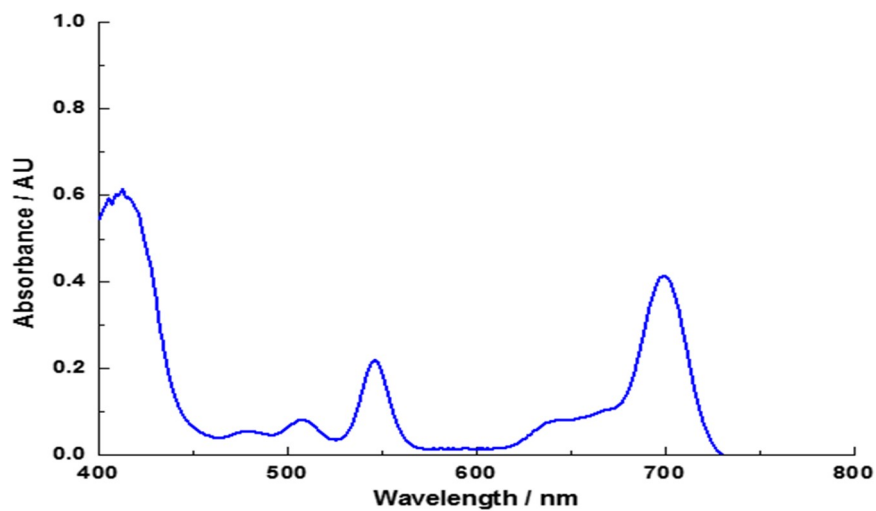
**Figure S1.**  $^1\text{H-NMR}$  spectrum of purpurin-18 (P18) (500 MHz,  $\text{CDCl}_3$ , 298 K).



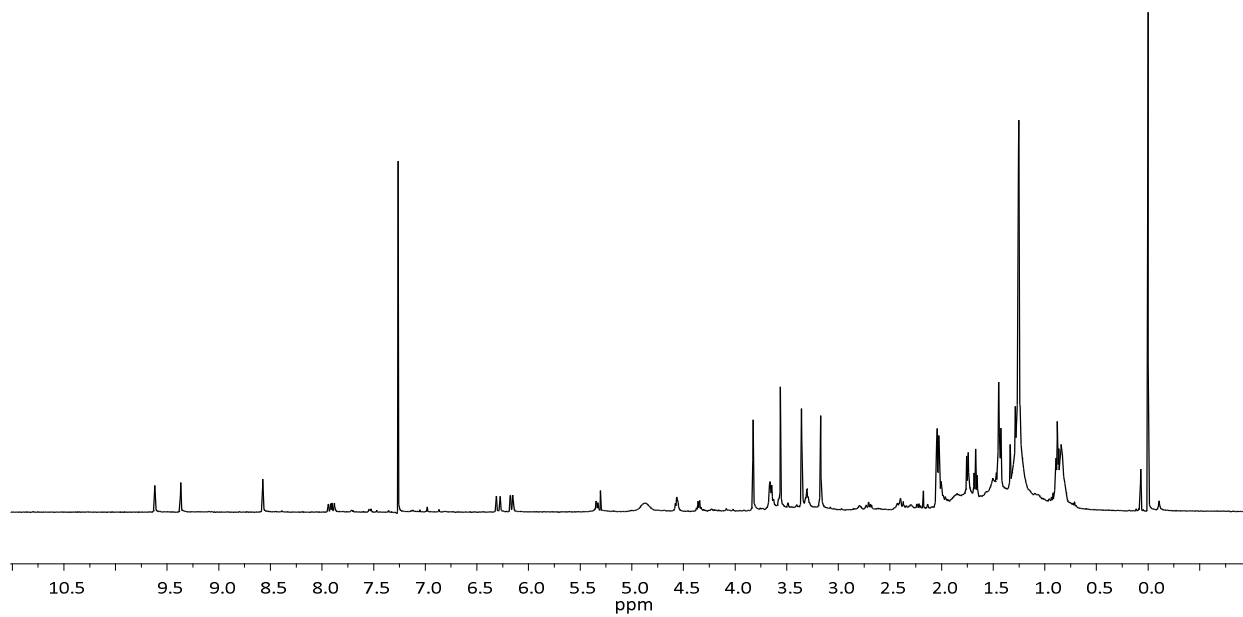
**Figure S2.** UV-Vis spectrum of purpurin-18 (P18) ( $\text{CH}_2\text{Cl}_2$ ).



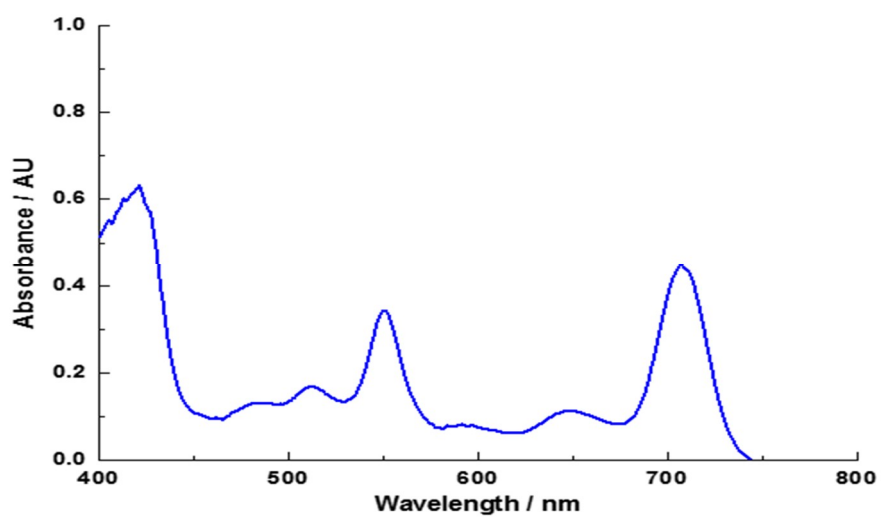
**Figure S3.**  $^1\text{H}$ -NMR spectrum of purpurin-18 methyl ester (P18ME) (500 MHz,  $\text{CDCl}_3$ , 298 K).



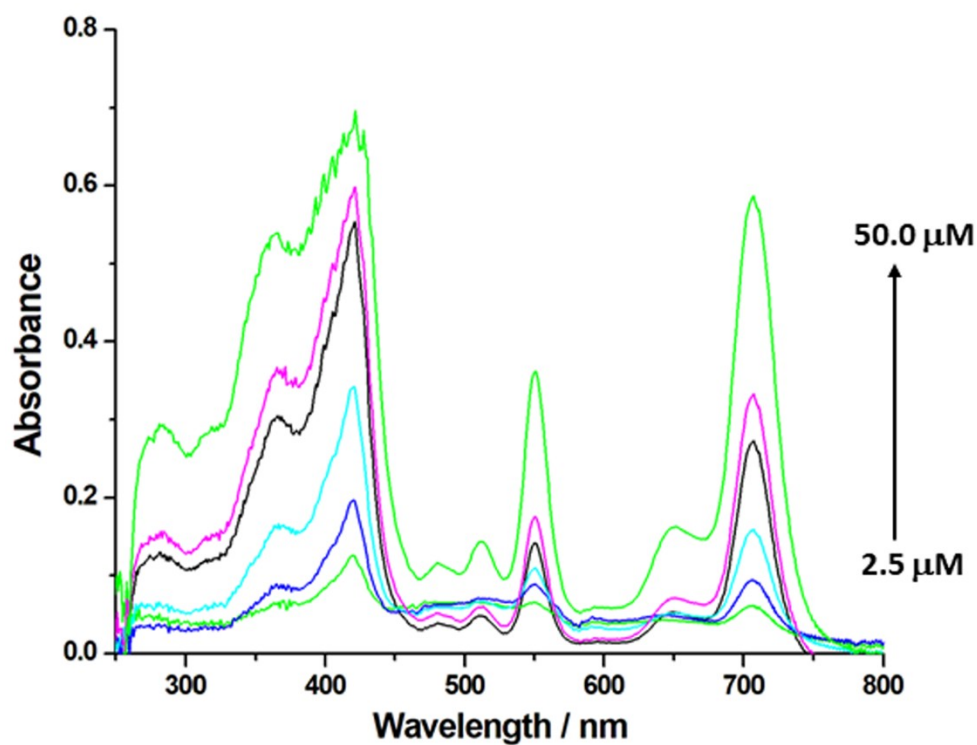
**Figure S4.** UV-Vis spectrum of purpurin-18 methyl ester (P18ME) ( $\text{CH}_2\text{Cl}_2$ ).



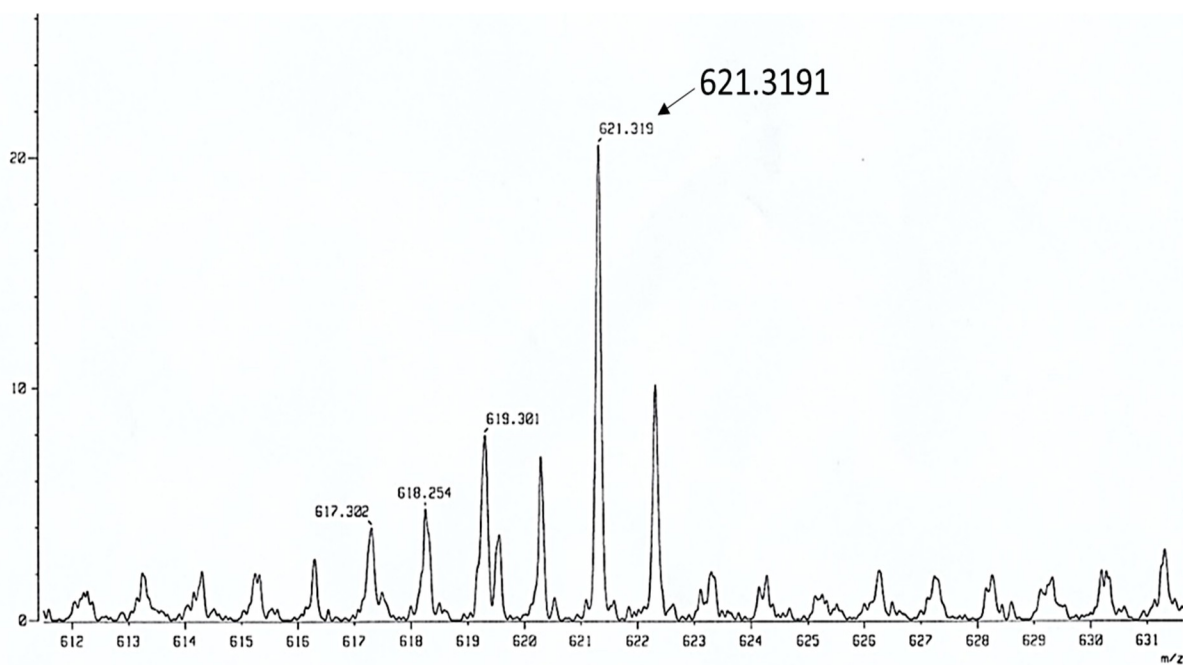
**Figure S5.**  $^1\text{H-NMR}$  spectrum of purpurin-18-*N*-ethylamine, PS **1** (500 MHz,  $\text{CDCl}_3$ , 298 K).



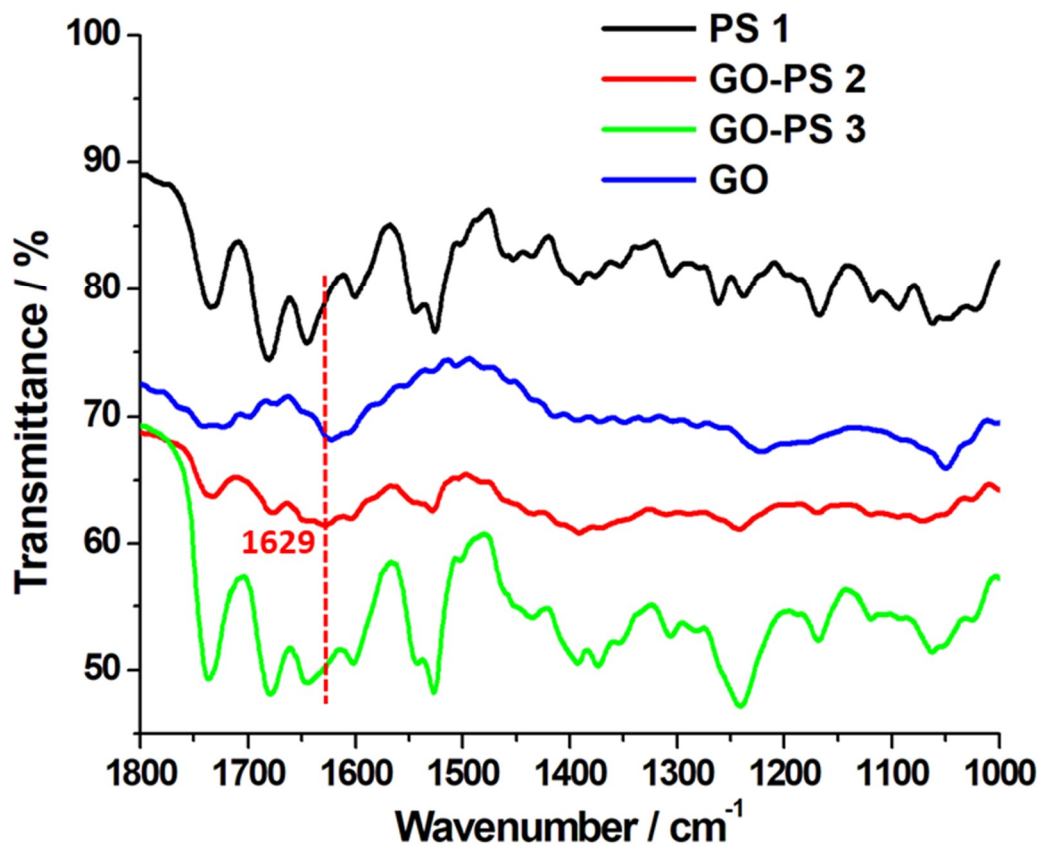
**Figure S6.** UV-Vis spectrum of purpurin-18-*N*-ethylamine, PS **1** ( $\text{CH}_2\text{Cl}_2$ ).



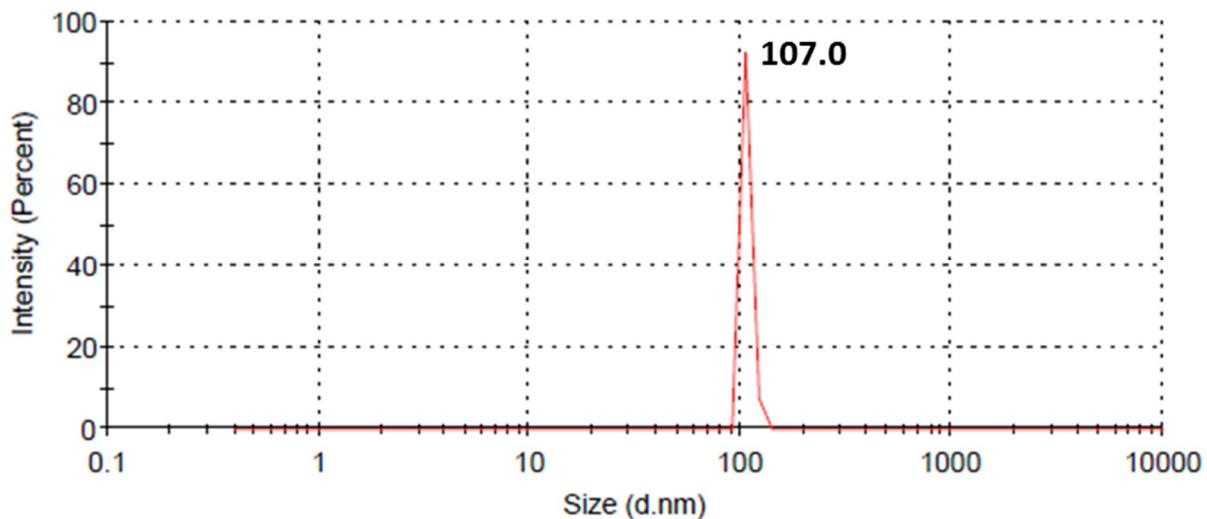
**Figure S7.** UV-Vis absorbance spectra of PS **1** at various concentrations of 2.5~50  $\mu\text{M}$  (DMSO).



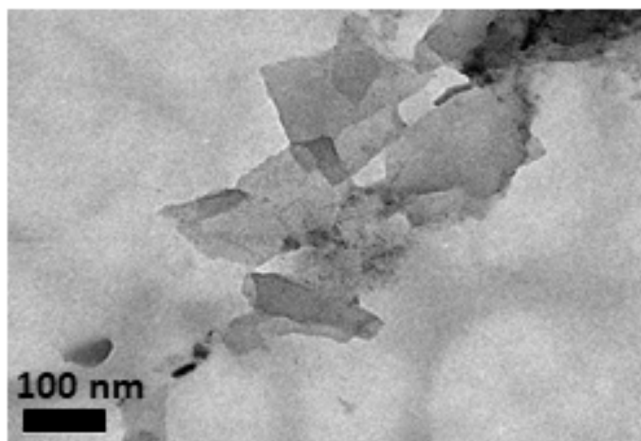
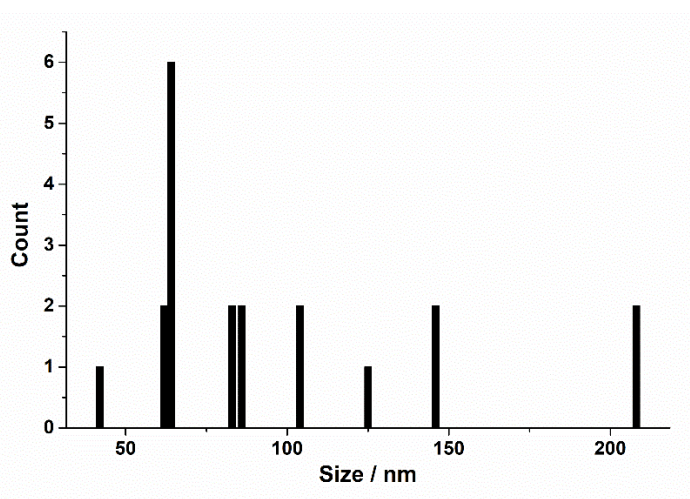
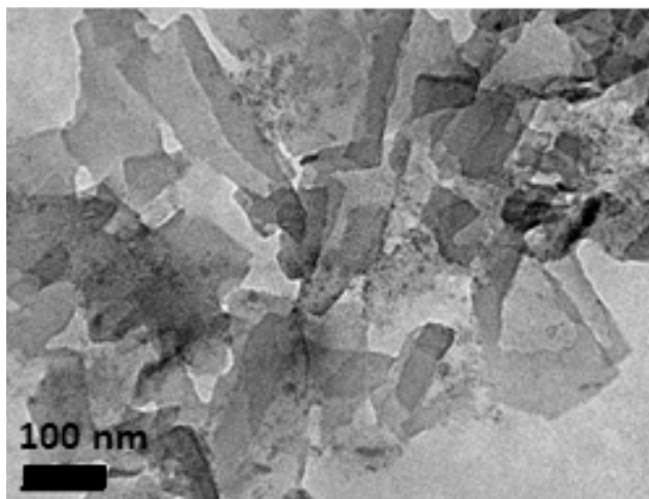
**Figure S8.** HRFABMS spectrum of PS **1**.



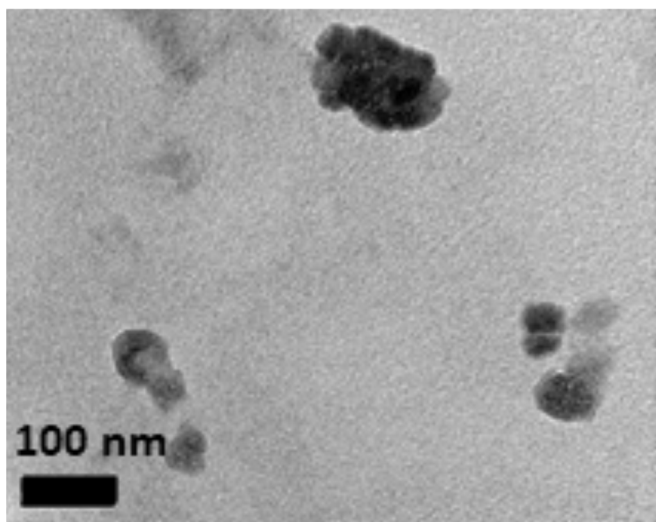
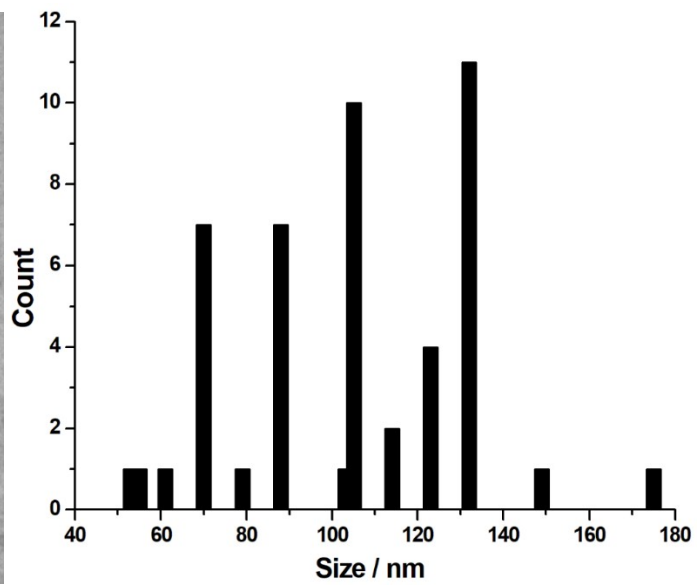
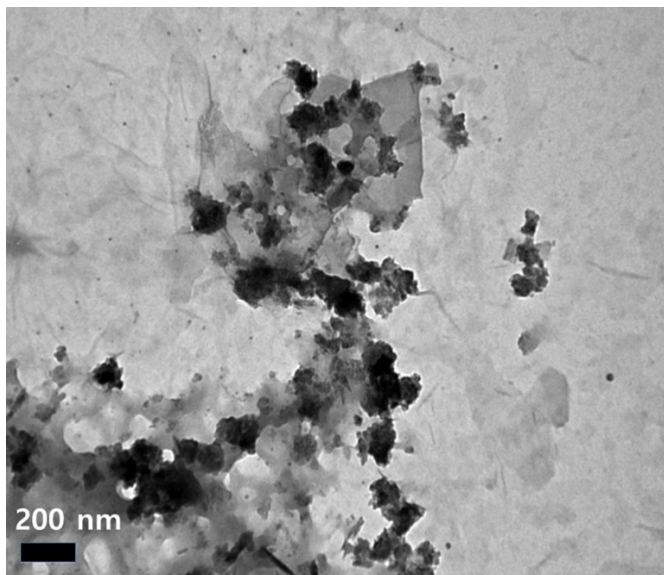
**Figure S9.** Extended FT-IR spectra of PS 1, GO-PS 2, GO-PS 3 and GO at 1800~1000  $\text{cm}^{-1}$ .



**Figure S10.** Size distribution of GO measured by dynamic light scattering. Average size is  $107.0 \pm 5.0$ .

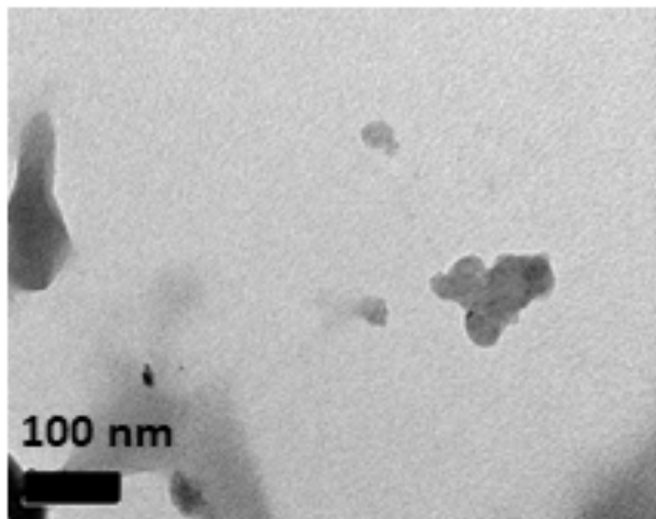
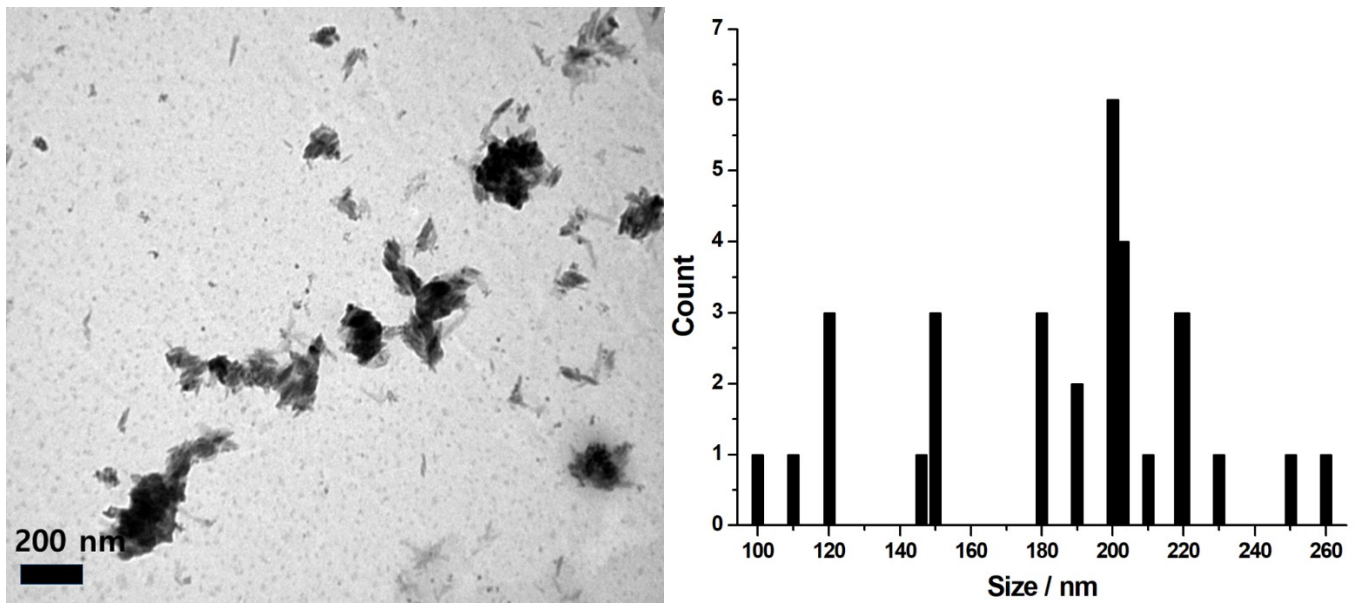


**Figure S11.** TEM images and size distribution of GO base on TEM images. Average size is  $96.1 \pm 47.7$  nm.



**Figure S12.** TEM images and size distribution of GO-PS 2 base on TEM images. Average size is  $104.2 \pm 27.1$  nm.





**Figure S13.** TEM images and size distribution of GO-PS **3** based on TEM images. Average size is  $187.2 \pm 40.1$  nm.

## In vitro photosensitizing effect

**Table S1.** Cell viability (%) of A549 cell only (control), PS **1**, GO-PS **2**, GO-PS **3**, GO(2) and GO(3) for photocytotoxicity against A549 cell lines. The concentration range of PS **1** was 1.0–20.0  $\mu\text{M}$ , and **2** and **3** have a concentration range of 1.4–14.0  $\mu\text{M}$ . The percentage of cell viability was conducted by MTT assay at (a) 3 h, (b) 12 h and (c) 24 h incubation times after irradiation. Error values represent the standard deviation of three replicate experiments.

		Incubation time	
<b>control</b>	3 h	100 $\pm$ 2.19	
	12 h	100 $\pm$ 1.22	
	24 h	100 $\pm$ 5.03	

	Incubation time	Concentration ( $\mu\text{M}$ )				
		1.0	2.5	5.0	10.0	20.0
<b>1</b>	3 h	100 $\pm$ 0.38	98.31 $\pm$ 3.40	80.48 $\pm$ 1.74	42.40 $\pm$ 2.82	21.44 $\pm$ 0.30
	12 h	100 $\pm$ 1.56	67.86 $\pm$ 2.11	36.94 $\pm$ 0.38	31.47 $\pm$ 1.51	11.96 $\pm$ 1.48
	24 h	50.43 $\pm$ 3.51	26.10 $\pm$ 1.02	19.43 $\pm$ 0.83	14.83 $\pm$ 0.75	6.72 $\pm$ 1.41

	Incubation time	Concentration ( $\mu\text{M}$ )			
		1.4	3.5	7.0	14.0
<b>2</b>	3 h	31.56 $\pm$ 1.77	24.21 $\pm$ 2.59	14.45 $\pm$ 1.71	16.50 $\pm$ 2.83
	12 h	14.42 $\pm$ 0.60	19.13 $\pm$ 2.26	10.88 $\pm$ 1.15	17.43 $\pm$ 3.05
	24 h	16.67 $\pm$ 1.67	7.76 $\pm$ 0.95	2.96 $\pm$ 0.65	2.78 $\pm$ 4.31
<b>3</b>	3 h	21.73 $\pm$ 1.29	21.12 $\pm$ 1.60	22.96 $\pm$ 0.97	23.85 $\pm$ 1.46
	12 h	22.39 $\pm$ 1.20	18.90 $\pm$ 0.20	15.62 $\pm$ 0.35	17.22 $\pm$ 0.21
	24 h	29.81 $\pm$ 0.66	25.28 $\pm$ 0.73	21.14 $\pm$ 1.25	20.32 $\pm$ 2.71
GO only	3 h	83.89 $\pm$ 4.57	83.66 $\pm$ 5.65	87.51 $\pm$ 3.98	78.76 $\pm$ 2.71
	12 h	86.14 $\pm$ 5.34	73.12 $\pm$ 9.18	75.34 $\pm$ 4.20	78.66 $\pm$ 5.37
	24 h	84.24 $\pm$ 6.72	82.56 $\pm$ 2.97	71.86 $\pm$ 7.48	67.96 $\pm$ 2.78

**Table S2.** Cell viability (%) of A549 cell only (control), PS **1**, GO–PS **2**, GO–PS **3**, GO(2) and GO(3) for dark cytotoxicity against A549 cell lines. The concentration range of PS **1** was 1.0–20.0  $\mu$ M, and **2** and **3** have a concentration range of 1.4–14.0  $\mu$ M. The percentage of cell viability was conducted by MTT assay at (a) 3 h, (b) 12 h and (c) 24 h incubation times no irradiation. Error values represent the standard deviation of three replicate experiments.

Incubation time		Concentration ( $\mu$ M)				
		1.0	2.5	5.0	10.0	20.0
<b>control</b>	3 h	100 $\pm$ 3.29				
	12 h	100 $\pm$ 0.72				
	24 h	100 $\pm$ 5.21				
Incubation time		Concentration ( $\mu$ M)				
		1.4	3.5	7.0	14.0	
<b>1</b>	3 h	100 $\pm$ 1.23	100 $\pm$ 2.36	100 $\pm$ 1.63	100 $\pm$ 2.88	83.98 $\pm$ 2.28
	12 h	100 $\pm$ 0.71	100 $\pm$ 2.61	100 $\pm$ 4.05	100 $\pm$ 0.68	80.89 $\pm$ 3.72
	24 h	100 $\pm$ 2.19	98.49 $\pm$ 1.90	100 $\pm$ 1.49	100 $\pm$ 3.74	59.72 $\pm$ 1.33
<b>2</b>	3 h	100 $\pm$ 4.77	100 $\pm$ 1.69	89.53 $\pm$ 4.70	70.78 $\pm$ 2.07	
	12 h	91.19 $\pm$ 3.28	84.08 $\pm$ 4.99	70.50 $\pm$ 6.23	56.36 $\pm$ 5.92	
	24 h	85.89 $\pm$ 4.02	78.99 $\pm$ 7.30	73.40 $\pm$ 6.18	61.22 $\pm$ 3.00	
<b>3</b>	3 h	100 $\pm$ 2.24	100 $\pm$ 3.37	100 $\pm$ 0.77	100 $\pm$ 4.10	
	12 h	100 $\pm$ 1.78	100 $\pm$ 3.04	100 $\pm$ 0.78	98.06 $\pm$ 2.05	
	24 h	100 $\pm$ 5.44	100 $\pm$ 2.31	100 $\pm$ 0.77	95.17 $\pm$ 3.55	
GO only	3 h	82.21 $\pm$ 2.75	81.51 $\pm$ 4.23	69.02 $\pm$ 3.76	65.26 $\pm$ 1.00	
	12 h	97.77 $\pm$ 4.45	95.76 $\pm$ 1.74	81.33 $\pm$ 3.36	58.57 $\pm$ 3.86	
	24 h	85.33 $\pm$ 6.60	85.92 $\pm$ 8.00	74.02 $\pm$ 4.87	67.91 $\pm$ 1.81	

**Table S3.** Cell viability (%) of A549 cell only (control), GO–PS **2** and GO–PS **3** for photocytotoxicity against A549 cell lines at low concentration. The concentration range of all compounds was 0.14 to 1.05  $\mu\text{M}$ . The percentage of cell viability was conducted by MTT assay at (a) 3 h, (b) 12 h and (c) 24 h incubation times after irradiation. Error values represent the standard deviation of three replicate experiments.

Incubation time		Concentration ( $\mu\text{M}$ )			
	Incubation time	0.14	0.35	0.70	1.05
		control	3 h	100 $\pm$ 3.82	
	12 h	100 $\pm$ 2.16			
	24 h	100 $\pm$ 5.70			
<b>2</b>	3 h	100 $\pm$ 3.74	74.54 $\pm$ 5.04	47.87 $\pm$ 3.45	26.55 $\pm$ 2.82
	12 h	100 $\pm$ 1.15	56.91 $\pm$ 0.70	34.44 $\pm$ 2.10	26.41 $\pm$ 1.68
	24 h	100 $\pm$ 4.55	36.27 $\pm$ 7.92	16.01 $\pm$ 2.47	11.71 $\pm$ 1.17
<b>3</b>	3 h	76.35 $\pm$ 0.28	1.77 $\pm$ 0.45	2.36 $\pm$ 1.20	11.50 $\pm$ 0.72
	12 h	67.16 $\pm$ 1.34	13.02 $\pm$ 0.70	12.65 $\pm$ 2.82	8.76 $\pm$ 4.66
	24 h	67.81 $\pm$ 9.78	6.58 $\pm$ 0.40	10.75 $\pm$ 3.80	6.83 $\pm$ 1.39