Supporting Information for

Triple-functional Core-Shell Structured Upconversion Luminescent Nanoparticles Covalently Grafted by Photosensitizer for Luminescent, Magnetic Resonance Imaging and Photodynamic Therapy in Vitro

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Figure S1. The concentration-dependent ultraviolet-visible absorption signal of PS molecule in DMF solution. ((a) based on the typical absorption of HP at about 400 nm and (b) based on the typical absorption of SPCD at about 668 nm).

Figure S2. The HRTEM image of NaGdF$_4$:Yb,Er NPs (a) and NaGdF$_4$:Yb,Er@CaF$_2$ NPs (b), HAADF-STEM image of NaGdF$_4$:Yb,Er@CaF$_2$ NPs (c) and upconversion luminescent spectra of NaGdF$_4$:Yb,Er and NaGdF$_4$:Yb,E@CaF$_2$ NPs (d).
**Figure S3.** The HeLa cells incubated with as-prepared nanomaterial \( \text{NaGdF}_4: \text{Yb,Er}@\text{CaF}_2 \)-SPCD and the corresponding upconversion emission spectra (b). The red and green lines correspond to the two areas. Fluorescent images acquired from 32 channels in 458-650 nm region (c). The number under each panel corresponds to the detected central spectral wavelength.
**Figure S4.** Confocal fluorescent images of HeLa cells incubated with as-prepared nanomaterial NaGdF$_4$:Yb,Er@CaF$_2$@SiO$_2$-SPCD of 0 and 100 µM after 5 min irradiation with power density of 0, 1.0, 1.7, 2.3, 2.4 and 2.5 W/cm$^2$ under 980 nm laser diode (in each sample a for fluorescent channel of CAM, b for channel of PI, c for bright-field and d for merged images of HeLa cells).
Figure S5. Confocal fluorescent images of HeLa cells incubated with as-prepared nanomaterial NaGdF₄:Yb,Er@CaF₂@SiO₂-SPCD with the concentration of 0, 50, 80 and 100 µM after 980 nm laser irradiation within 5 or 10 min with power density of 2.5 W/cm² (in each sample a for fluorescent channel of CAM, b for channel of PI, c for bright-field and d for merged images of HeLa cells).
**Figure S6.** The time-dependent temperature in HeLa cell medium under the irradiation of 980 nm laser diode with power density of 2.5 W/cm².

**Figure S7.** Transverse relaxivities ($r_2$) data (fitting curve) of as-prepared nanomaterials (NaGdF₄:Yb,Er@CaF₂@SiO₂-PS) and commercial contrast agent Gd-DTPA aqueous solution, and $T_2$-weighted MR images of nanomaterials aqueous solution with Gd³⁺ ion concentration from 0.1 to 0.3 mM (D4= 200 ms).

**Table S1.** The electronic longitudinal ($T_1$) and transverse relaxation ($T_2$) time of as-prepared nanomaterial NaGdF₄:Yb,Er@CaF₂@SiO₂-HP, NaGdF₄:Yb,Er@CaF₂@SiO₂-SPCD and commercial contrast agent (Gd-DTPA). The last row for the ratio of longitudinal relaxivities value ($r_1$) to transverse relaxivities value ($r_2$).

<table>
<thead>
<tr>
<th>Gd³⁺ (mM)</th>
<th>Gd-DTPA</th>
<th>HP-grafted nanomaterial</th>
<th>SPCD-grafted nanomaterial</th>
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<tbody>
<tr>
<td></td>
<td>$T_1$ (ms)</td>
<td>$T_2$ (ms)</td>
<td>$T_1$ (ms)</td>
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<td>/</td>
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<td>2401</td>
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<td>473</td>
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</tr>
<tr>
<td>0.50</td>
<td>/</td>
<td>/</td>
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$\frac{r_1}{r_2}$: 0.85 1.62 1.67