Supporting Information for

An efficient dye-sensitized NIR emissive lanthanide nanomaterial and its application in fluorescence-guided peritumoral lymph node dissection

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Figure S1. The energy transfer pathways in the dye-sensitized core/shell nanoparticles.

Figure S2. FTIR spectra of Cy7, PC, OA-CS nanoparticles and CS&Cy7@PC nanoparticles.
**Figure S3.** The emission spectra of nanoparticles with the concentration of (a) Cy7 and (b) ICG varying from 0 μM to 4 μM (left) and from 5 μM to 20 μM (right) in EtOH under the excitation of an 808 nm laser (2 W/cm²).

**Figure S4.** (a) The emission spectra of Cy7 with varied concentrations of Cy7 in sensitization system in EtOH under the excitation of a 760 nm Xe lamp. (b) The emission intensity of Yb³⁺ and Cy7 from dye-sensitized LnNPs versus the Cy7 concentration.
**Figure S5.** The emission spectra of NaYF₄:Yb,Nd@CaF₂ with the concentration of Cy7 varying from 0 μM to 5 μM in EtOH under the excitation of an 808 nm laser (2 W/cm²).

**Figure S6.** XRD patterns of the nanoparticles NaYbF₄ and NaYbF₄@NaYF₄:x%Nd(x=20, 40, 60).
Figure S7. The standard concentration curves of (a) Y$^{3+}$ ions and (b) Nd$^{3+}$ ions; (c) The experimental concentration of Y$^{3+}$ and Nd$^{3+}$ ions in different nanoparticles.

![Graphs showing concentration curves for Y$^{3+}$ and Nd$^{3+}$ ions](image1)

<table>
<thead>
<tr>
<th></th>
<th>Y $\mu$mol/L</th>
<th>Nd $\mu$mol/L</th>
<th>Y+Nd $\mu$mol/L</th>
<th>Y (%)</th>
<th>Nd (%)</th>
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<tr>
<td>NaYbF$_4$@NaYF$_4$: 20%Nd</td>
<td>1104.414</td>
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<td>NaYbF$_4$@NaYF$_4$: 40%Nd</td>
<td>835.317</td>
<td>397.331</td>
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<td>NaYbF$_4$@NaYF$_4$: 60%Nd</td>
<td>598.8</td>
<td>668.221</td>
<td>1267.021</td>
<td>47.2%</td>
<td>52.7%</td>
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</tbody>
</table>

Figure S8. (a) TEM image of NaYbF$_4$@NaYF$_4$:80%Nd. (b) The emission spectra of NaYbF$_4$@NaYF$_4$:x%Nd (x=20, 40, 60, 80), excited by 808 nm laser (2 W/cm$^2$).
Figure S9. The emission spectra of (a) NaYbF₄@NaYF₄:20%Nd, (b) NaYbF₄@NaYF₄:40%Nd, (c) NaYbF₄@NaYF₄:60%Nd with the concentration of Cy7 varying from 0 µM to 4 µM (left) and from 5 µM to 15 µM (right) in EtOH under the excitation of an 808 nm laser (2 W/cm²).
Figure S10. (a) Schematic presentation of synthesis procedure of CS&Cy7@PC. (b) The emission spectra of CS&Cy7@PC with the concentration of Cy7 varying from 0 to 10 μM in EtOH under the excitation of a 808 nm laser (2 W/cm²). Insert shows the emission intensity of 980 nm from CS&Cy7@PC versus the Cy7 concentration. (c) TEM image of CS&Cy7@PC. (d) Dynamic Light Scattering (DLS) of OA capped nanoparticles and PC wrapped hybrid materials, respectively.
Figure S11. (a) The emission spectra of CS&Cy7@PC with varied concentrations of Cy7 for sensitization in water under the excitation of a 760 nm Xe lamp; (c) The emission intensity of Yb$^{3+}$ and Cy7 from CS&Cy7@PC versus the Cy7 concentration.

**Calculation of relative quantum yield:** The relative quantum yield of samples are calculated according to the previous literature. Indocyanine green (ICG) in DMSO was chosen as the standard sample, whose quantum yield is 13.2% as we all know. Each sample was required to record the UV-vis absorbance spectrum and fluorescence spectrum for five solutions with increasing concentrations. Plot a graph of integrated fluorescence intensity vs absorbance. The unknown values are calculated using the standard samples which have a fixed and known fluorescence quantum yield value, according to the following equation:

$$\Phi_X = \Phi_{ST} \left( \frac{\text{Gradient}_X}{\text{Gradient}_{ST}} \right) \left( \frac{\eta_X}{\eta_{ST}} \right)$$

Where the subscripts ST and X denote standard and text respectively, $\Phi$ is the quantum yield, Gradient is the gradient from the plot of fluorescence intensity vs absorbance, and $\eta$ is the refractive index of the solvent.

![Graph](image)

Figure S12. (a) Linear plots for Cy7 (sample) and ICG (standard), respectively; (b) The QY of ICG, Cy7, ICG-sensitized nanoparticles and Cy7-sensitized nanoparticles in EtOH solutions were calculated in the same way, as well as the Cy7 wrapped in PC in water.

![Chemical structures](image)
**Figure S13.** The synthetic route of Cy7.

**Figure S14.** $^1$H NMR spectrum of Cy7 in the MeOD. $^1$H NMR (400 MHz, MeOD) δ 8.44 (d, J = 14.2 Hz, 2H), 7.51 (d, J = 7.4 Hz, 2H), 7.44 – 7.38 (m, 4H), 7.37 – 7.26 (m, 2H), 6.47 (d, J = 14.1 Hz, 2H), 4.45 – 4.41 (m, 4H), 2.76 – 2.70 (m, 8H), 1.94 (dd, J = 11.2, 5.9 Hz, 2H), 1.73 (s, 12H).
Figure S15. $^{13}$C NMR spectrum of Cy7 in MeOD.
Figure S16. MALDI-TOF MS Spectrum of compound Cy7. MS (MALDI-TOF-MS): calcd. For C$_{36}$H$_4$N$_2$O$_4$ $^+$. 599.27 [M]$^+$, found 599.26 [M]$^+$. 