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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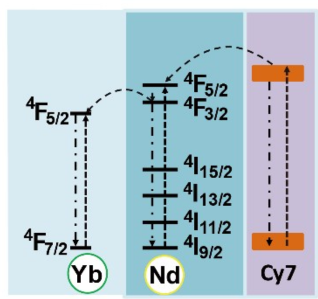


Figure S1. The energy transfer pathways in the dye-sensitized core/shell nanoparticles.

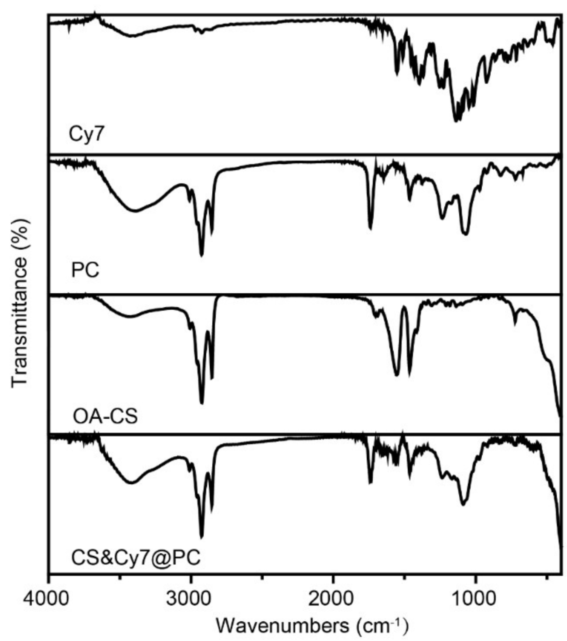


Figure S2. FTIR spectra of Cy7, PC, OA-CS nanoparticles and CS&Cy7@PC nanoparticles.

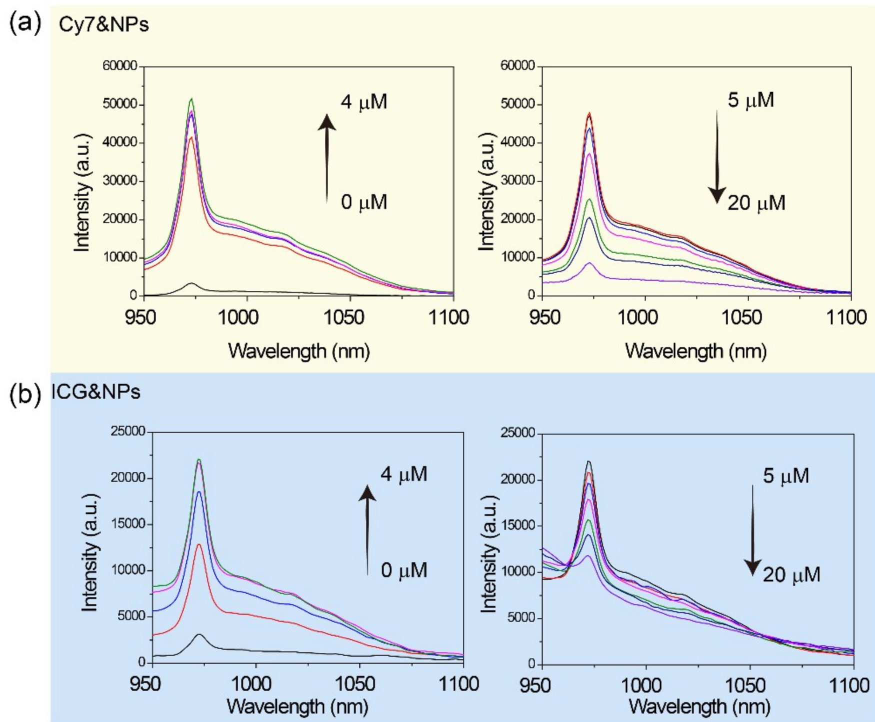


Figure S3. The emission spectra of nanoparticles with the concentration of (a) Cy7 and (b) ICG varying from 0 μM to 4 μM (left) and from 5 μM to 20 μM (right) in EtOH under the excitation of an 808 nm laser (2 W/cm^2).

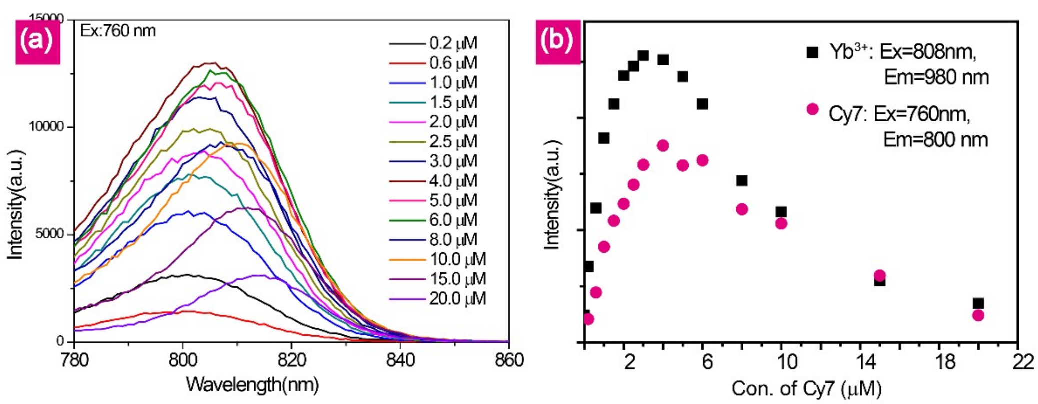


Figure S4. (a) The emission spectra of Cy7 with varied concentrations of Cy7 in sensitization system in EtOH under the excitation of a 760 nm Xe lamp. (b) The emission intensity of Yb^{3+} and Cy7 from dye-sensitized LnNPs versus the Cy7 concentration.

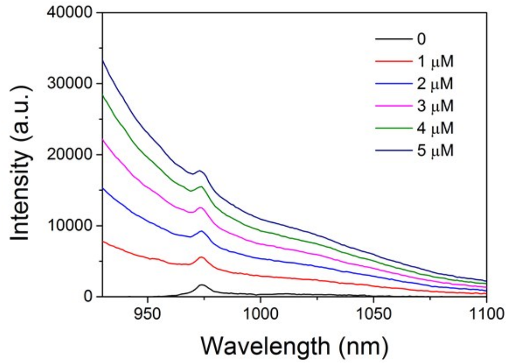


Figure S5. The emission spectra of $NaYF_4$:Yb,Nd@CaF_2 with the concentration of Cy7 varying from 0 μM to 5 μM in EtOH under the excitation of an 808 nm laser (2 W/cm^2).

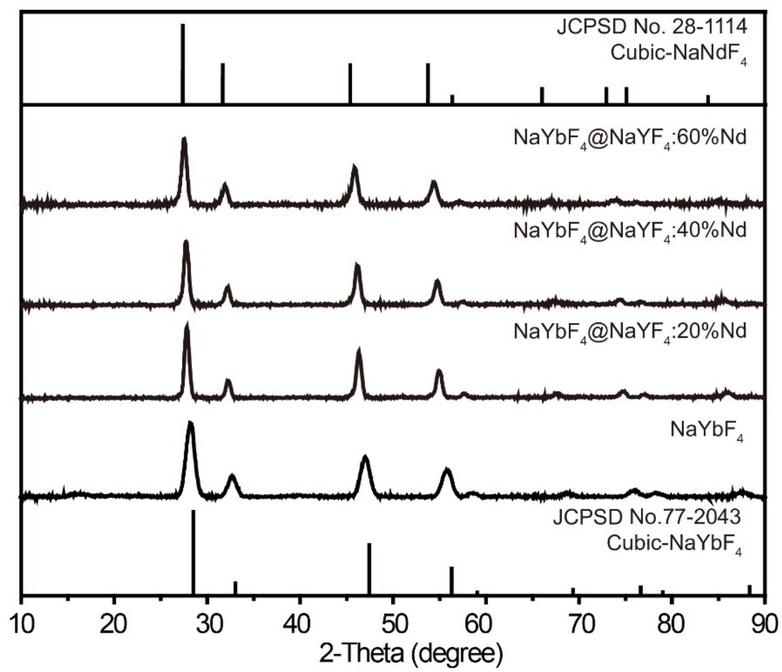
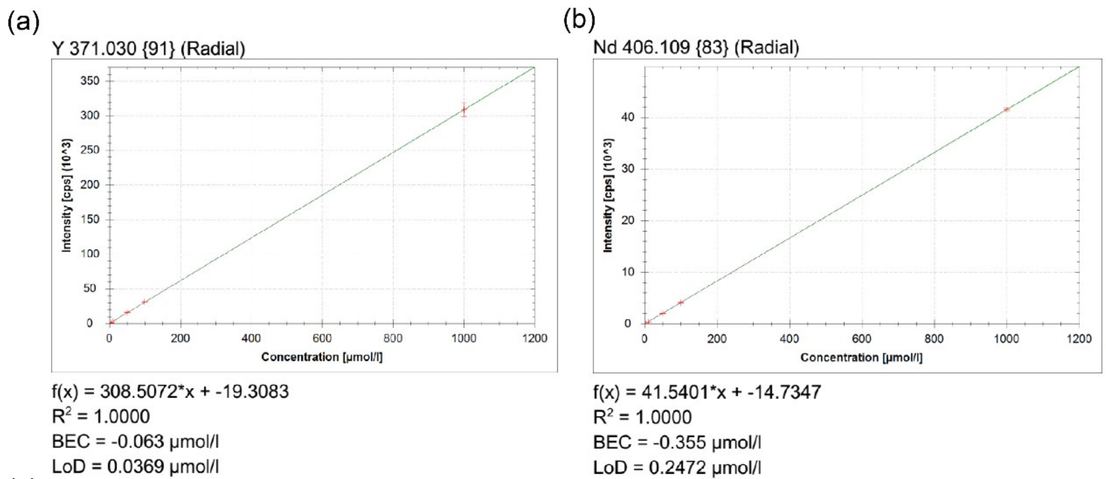


Figure S6. XRD patterns of the nanoparticles $NaYbF_4$ and $NaYbF_4$@$NaYF_4$:x%Nd(x=20, 40, 60).



(c)

	Y μmol/L	Nd μmol/L	Y+Nd μmol/L	Y	Nd
$NaYbF_4$@$NaYF_4$: 20%Nd	1104.414	188.643	1293.057	85.4%	14.6%
$NaYbF_4$@$NaYF_4$: 40%Nd	835.317	397.331	1232.648	67.8%	32.2%
$NaYbF_4$@$NaYF_4$: 60%Nd	598.8	668.221	1267.021	47.2%	52.7%

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.

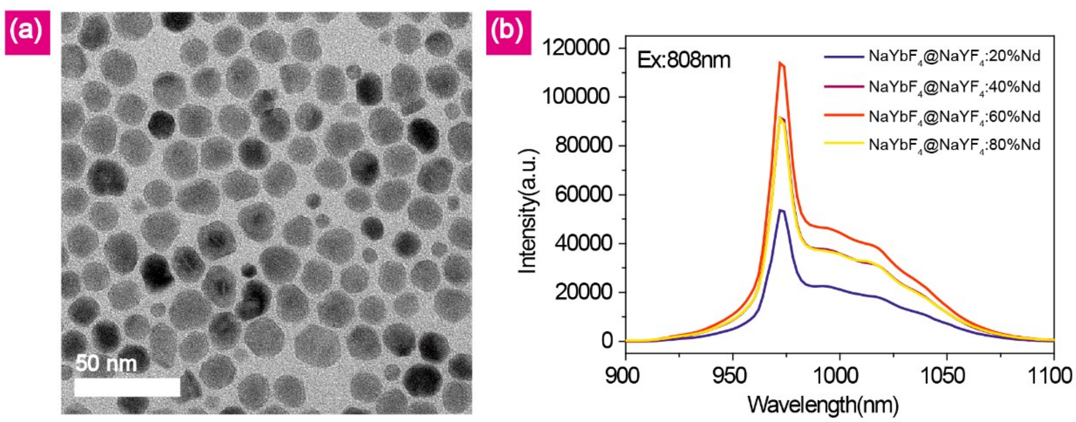


Figure S8. (a) TEM image of $NaYbF_4$@$NaYF_4$:80%Nd. (b) The emission spectra of $NaYbF_4$@$NaYF_4$:x%Nd (x=20, 40, 60, 80), excited by 808 nm laser (2 W/cm^2).

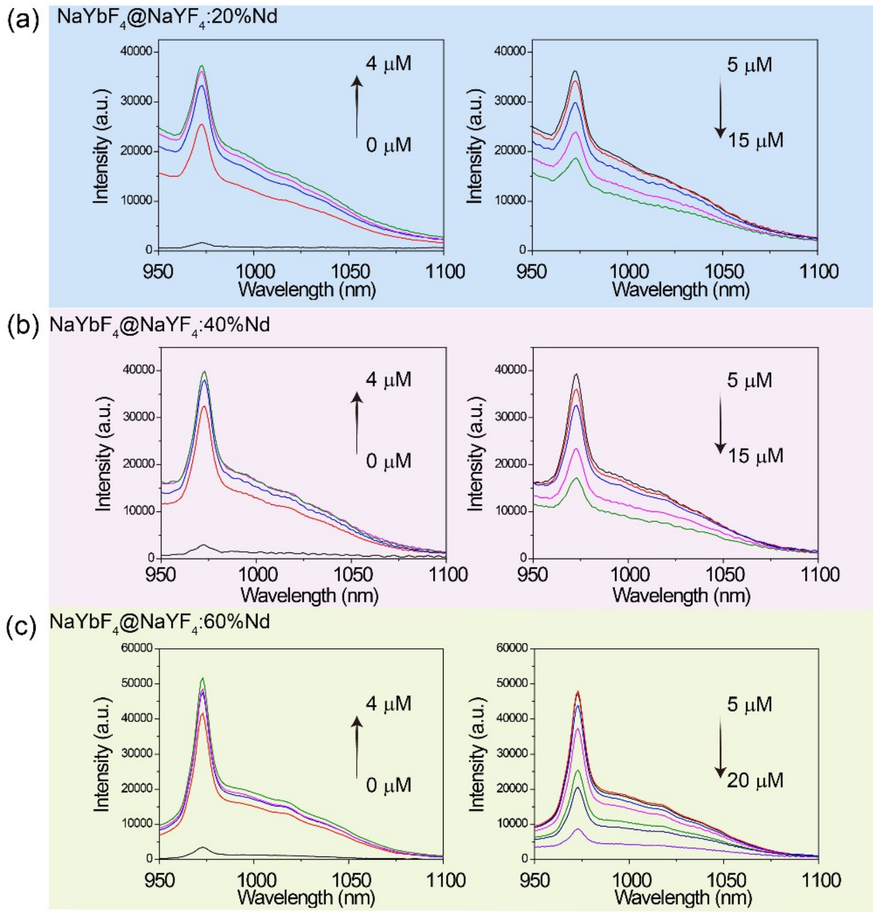


Figure S9. The emission spectra of (a) $NaYbF_4$@$NaYF_4$:20%Nd, (b) $NaYbF_4$@$NaYF_4$:40%Nd, (c) $NaYbF_4$@$NaYF_4$:60%Nd with the concentration of Cy7 varying from 0 μM to 4 μM (left) and from 5 μM to 15 μM (right) in EtOH under the excitation of an 808 nm laser (2 W/cm^2).

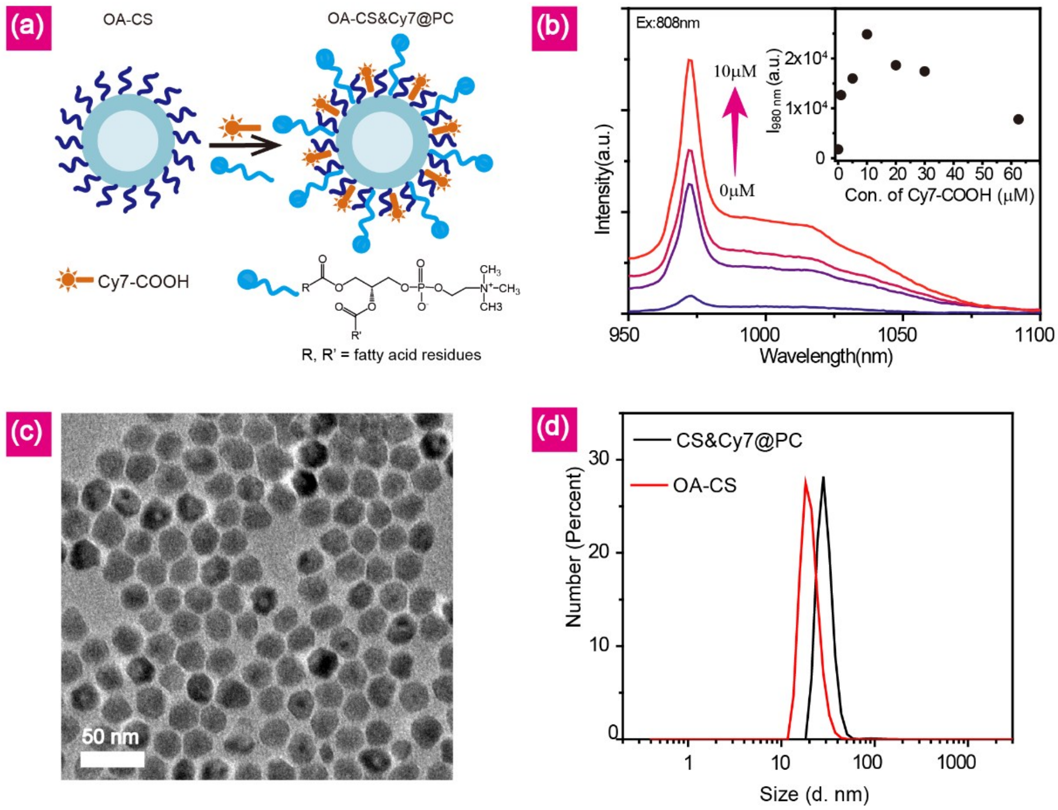


Figure S10. (a) Schematic presentation of synthesis procedure of CS&Cy7@PC. (b) The emission spectra of CS&Cy7@PC with the concentration of Cy7 varying from 0 to 10 μM in EtOH under the excitation of a 808 nm laser (2 W/cm^2). Insert shows the emission intensity of 980 nm from CS&Cy7@PC versus the Cy7 concentration. (c) TEM image of CS&Cy7@PC. (d) Dynamic Light Scattering (DLS) of OA capped nanoparticles and PC wrapped hybrid materials, respectively.

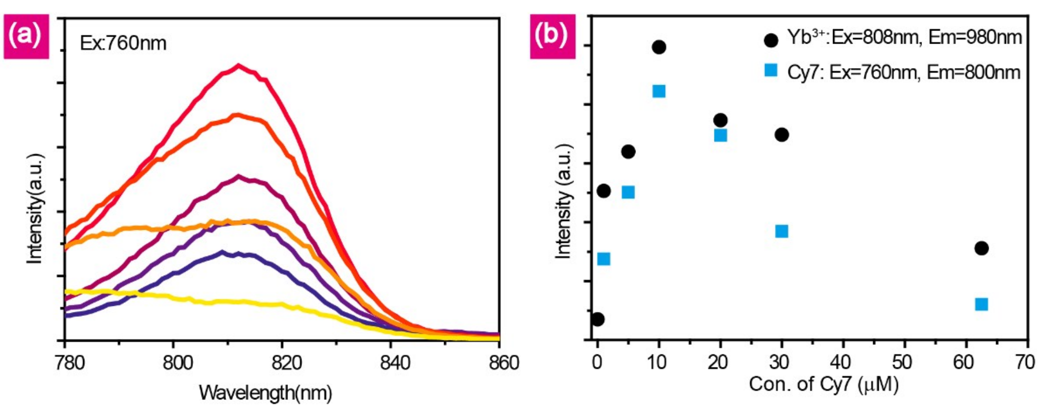
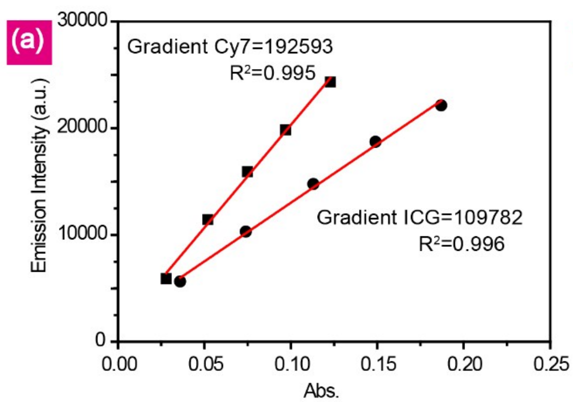


Figure S11. (a) The emission spectra of CS&Cy7@PC with varied concentrations of Cy7 for sensitization in water under the excitation of a 760 nm Xe lamp; (c) The emission intensity of Yb^{3+} and Cy7 from CS&Cy7@PC versus the Cy7 concentration.

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:

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

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



(b)

Materials	Gradient	Relative QY
ICG, DMSO	109782	13.2%
ICG, EtOH	126392	12.9%
Cy7, EtOH	192593	19.7%
CS&Cy7, EtOH	67008	6.9%
CS&ICG, EtOH	39479	4.9%
Cy7@PC, H_2O	75550	7.4%

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.

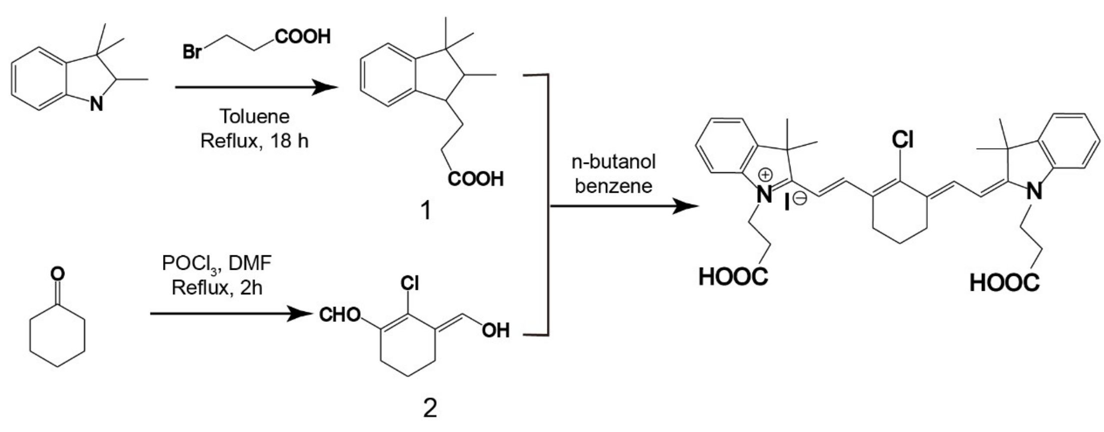


Figure S13. The synthetic route of Cy7.

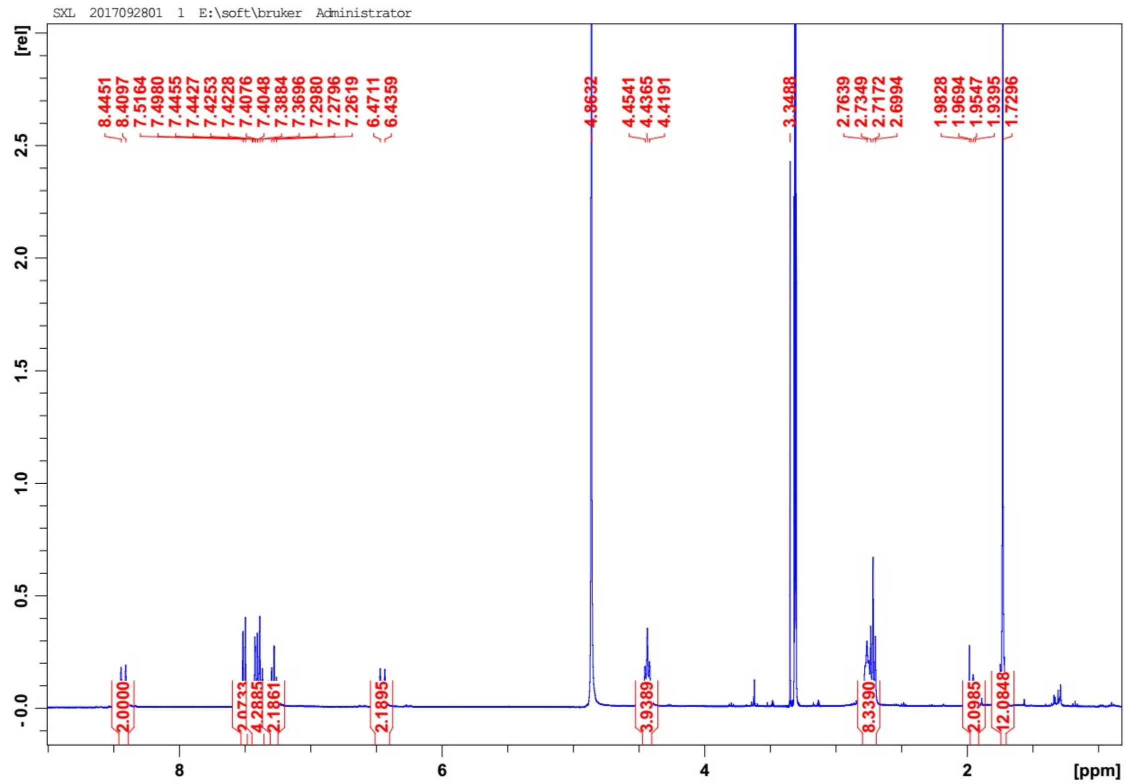


Figure S14. ^{1}H NMR spectrum of Cy7 in the MeOD. ^{1}H NMR (400 MHz, MeOD) δ 8.44 (d, J = 14.2 Hz, 2H), 7.51 (d, J = 7.4 Hz, 2H), 7.44 – 7.38 (m, 4H), 7.37 – 7.26 (m, 2H), 6.47 (d, J = 14.1 Hz,2H), 4.45 – 4.41 (m, 4H), 2.76 – 2.70 (m, 8H), 1.94 (dd, J = 11.2, 5.9 Hz 2H), 1.73 (s, 12H).

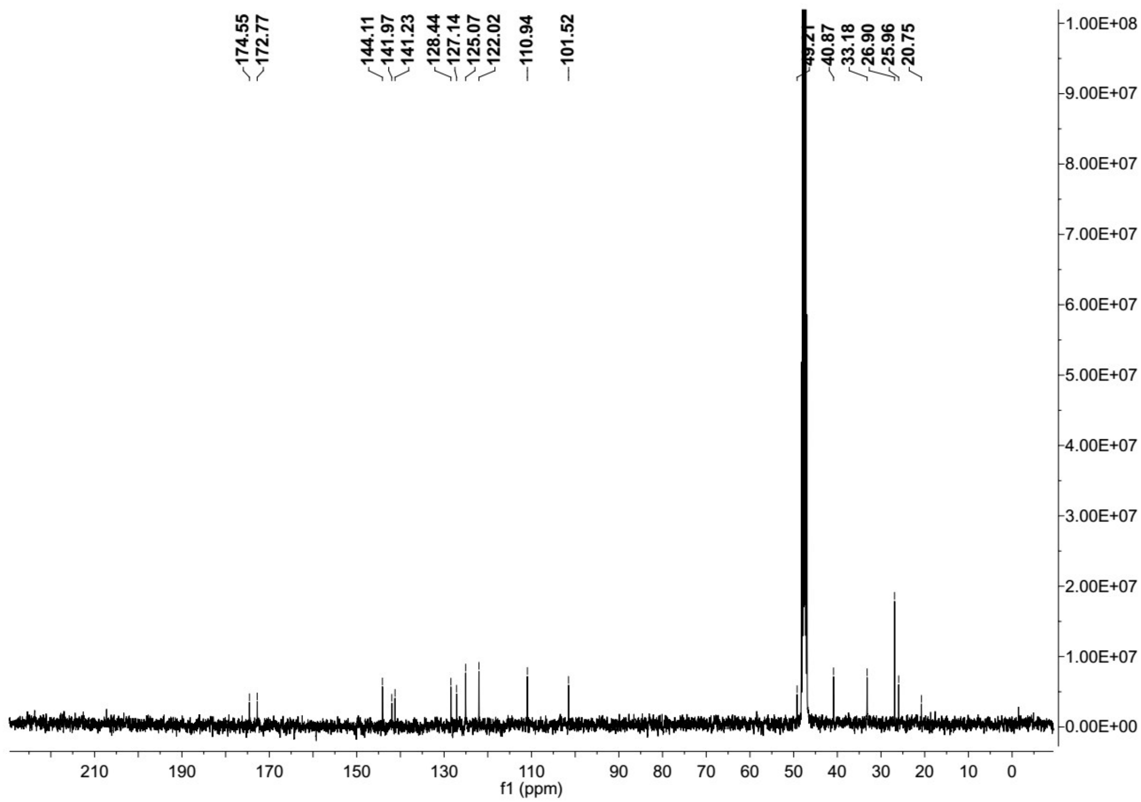


Figure S15. ^{13}C NMR spectrum of Cy7 in MeOD.

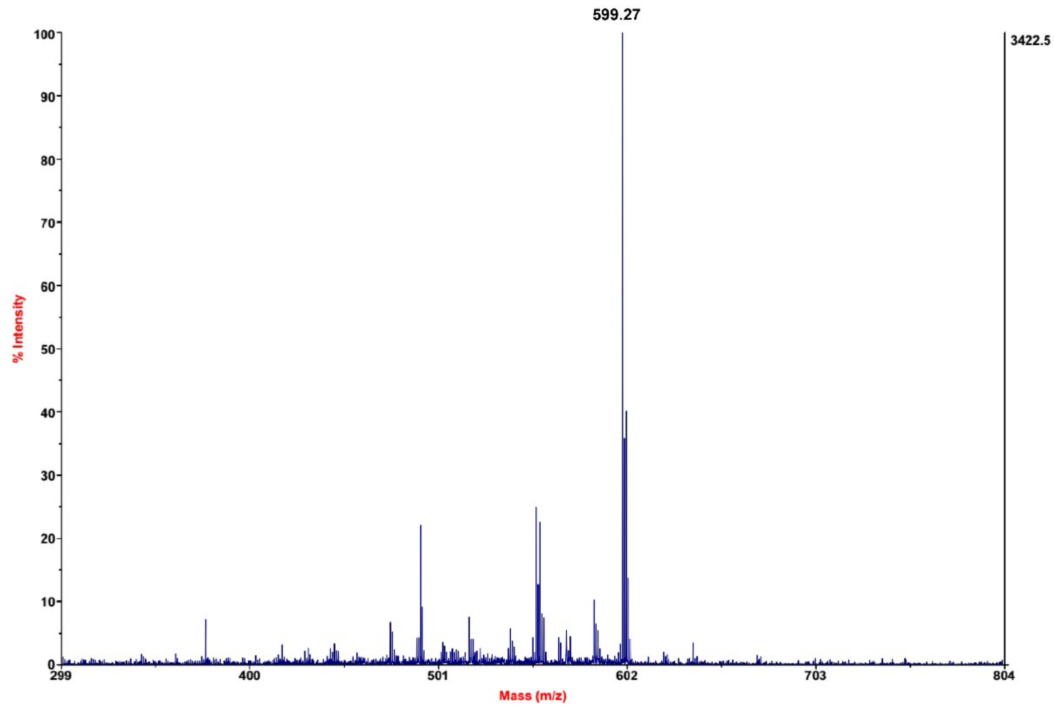


Figure S16. MALDI-TOF MS Spectrum of compound Cy7. MS (MALDI-TOF-MS): calcd. For $C_{36}H_4N_2O_4^+$ 599.27 [M]$^+$, found 599.26 [M]$^+$.