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双光子敏化 Eu^{3+}高效发光活细胞成像纳米生物探针

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Nanoprobes with Enhanced Two-Photon-Sensitized Eu^{3+} Luminescence Properties for Live Cell Imaging

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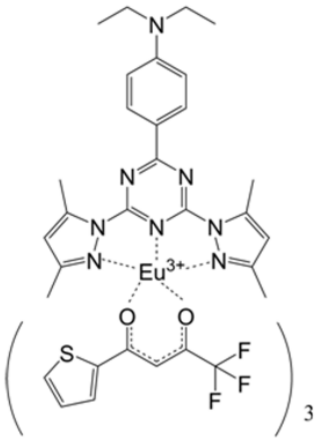
1. Components Analysis of EuPHS

The colloidal solution of EuPHS (30 mL) was centrifuged at 40,000 g, and then the precipitate of EuPHS was re-dispersed in water. This process was repeated twice, and then the precipitate of EuPHS was dried by keeping it with P_2O_5 in a desiccator for 15 h. The dried nanoparticles were dispersed in 0.6 mL acetone under sonication for 30 min and the mixture was kept for 24 h. In this process, the nanoparticles were swollen, and OTS in the nanoparticles was extracted into the solution. The obtained acetone dispersion was separated to two parts. One part of the dispersion was mixed with equal volume of methanol and the mixture was centrifuged at 10,000 g. Then, the supernate containing unhydrolysed OTS was quantitatively analyzed by gas chromatography. Another part of the acetone dispersion was used to determine the summation of Si in poly(octylsiloxane) and unhydrolysed OTS by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The molar ratio of OTS to hydrolysed OTS in EuPHS was determined to be 1:4.

The as-prepared EuPHS were washed thrice by centrifuging at 40,000 g with water and dried in a vacuum oven at 40 °C over night. The elemental compositions of C, H and N of EuPHS were measured by elemental analyzer (VARIO EL, Elementar Analysensysteme GmbH). The concentration of Eu and Si in the prepared EuPHS colloidal solutions without large particles was determined by ICP. The contents of $Eu(tta)_3dpbt$ and P(ST-co-MMA) in EuPHS could be calculated to be about 40% and 15%, respectively, according to the aforementioned data.

2. Numbers of $Eu(tta)_3dpbt$ molecules in a EuPHS

The density of EuPHS was estimated to be 1.0 g cm^{-3} according to the densities of P(ST-co-MMA) (1.05 g cm^{-3}), OTS (0.91 g cm^{-3}) and $Eu(tta)_3dpbt$ (0.92 g cm^{-3}), and the composition of EuPHS. The mass of a nanoparticle with an average diameter of 45 nm was calculated as 4.9×10^{-17}g, according to $m=V\times\rho$ where $V=\pi\times d_{av}^3/6$. Therefore, the number of $Eu(tta)_3dpbt$ molecules in a EuPHS particle of 45 nm could be calculated to be 1.0×10^4 $[(m\times40\%/M)\times N_A]$.



Sch.S1. Molecular structure of Eu(tta)$_3$dpbt.

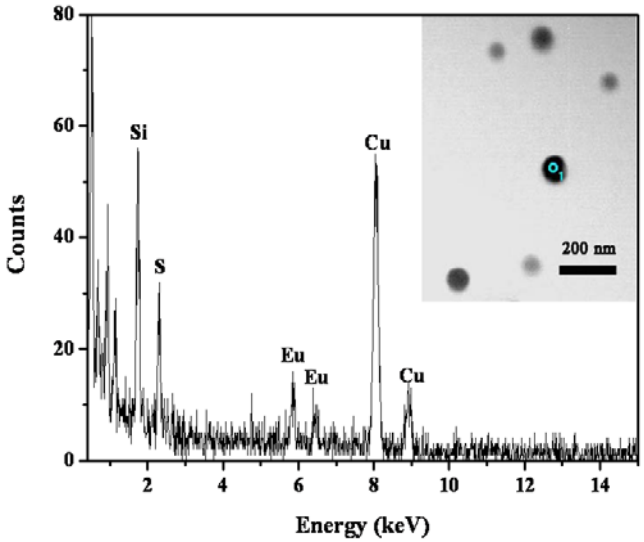


Fig.S1. EDX spectrum taken from the position marked with blue color in the STEM image of EuPHS (inset).

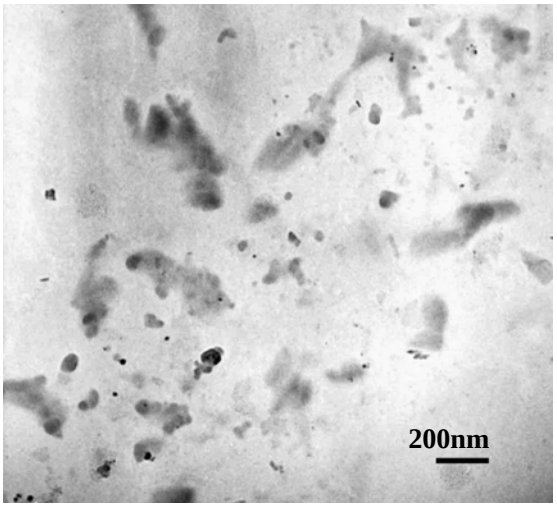


Fig.S2. TEM image of the nanoparticles prepared in the absence of OTS.

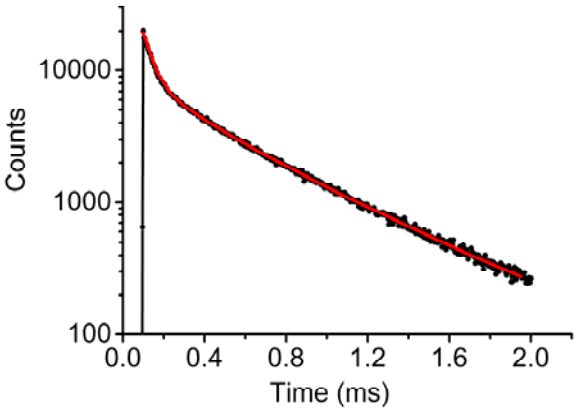


Fig.S3. Photoluminescence decay curve of EuPHS (λ_{ex}: 415 nm) at 614 nm (black line). The curve was fit with a two exponential decay model function, which yielded the apparent decay time constants of 51 μs (8%) and 508 μs (92%) (red line).

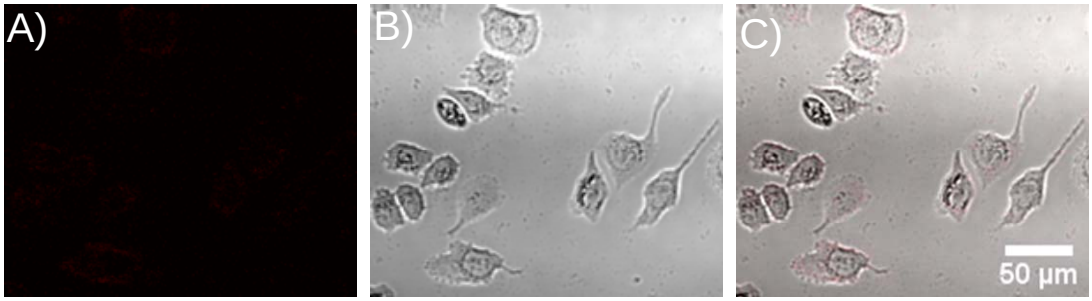


Fig.S4. Images of live HeLa cells pre-incubated in PBS buffer solution for 10 min, and then in a PBS buffer solution containing 10 mM of NaN_3 and 50 mM of 2-deoxy-d-glucose for 30 min at 37 °C, followed by incubation in a colloidal solution of Tf@EuPHS for 3 h at 37 °C.
a) Two-photon-excited luminescence images; b) Differential interference contrast (DIC) images; c) The overlay of the corresponding luminescence and DIC images. Images shown in panel of a-c have the same scale bar.