Supporting Information

1. The quasi-equilibrium times and duty cycle of CsPbBr₃ NCs and CsPbBr₃@Biotin probes

To determine the time that the nanocrystals need to reach the quasi-equilibrium between on and off states, CsPbBr₃ NCs were attached onto the bottom of an eight chambered NuncTM Lab-TekTM II Chamber SlideTM and excited by a 488 nm laser. Then, 30000 frames of fluorescent images were collected. The exposure time was set to be 20 ms per frame. Time-dependent fluorescence intensity profiles of CsPbBr₃ NCs were obtained by analyzing the 30000 frames of fluorescent images. Finally, we used 1500 frames as a group to monitor the changes in the on-off duty cycle as a function of imaging time. The result was shown in Figure S1. As we can see, more than 500 s was necessary to reach the quasi-equilibrium between on and off states. The average duty cycle of CsPbBr₃ NCs measured between 500–600 s is 0.0497.

Similarly, the time that CsPbBr₃@Biotin needed to reach the quasi-equilibrium state was determined in the same way, which is about 400 s (Figure S8). The average duty cycle of CsPbBr₃@Biotin measured between 400–500 s is 0.0245.

2. The localization precision of CsPbBr₃ NCs, CdSSe/ZnS QDs, ZnCdSe/ZnS QDs and CsPbBr₃@Biotin probes

The localization precision is determined by the following equation: $\Delta x = \sqrt{\frac{s^2 + \frac{a^2}{12}}{N} + \frac{8\pi s^4 b^2}{a^2 N^2}}$, where Δx is the localization precision; *s* is the standard deviation of PSF, which is related to the numerical aperture (NA) of the objective, *a* is the pixel size, *N* is the number of collected photons, and b is the background noise per pixel. To calculate the localization precision, CsPbBr₃ NCs were attached onto the bottom of an eight chambered NuncTM Lab-TekTM II Chamber SlideTM and excited by a 488 nm laser. Then, 10000 frames of fluorescent images with an imaging size of 12.8×12.8 µm were collected by a 100× (NA = 1.46) oil immersion objective and recorded by an Andor EM-CCD camera (iXon DU897). The exposure time was set to be 20 ms per

frame. The localization precision is calculated according to the above equation using the Zeiss Zen 2012 software.

The localization precision of CdSSe/ZnS QDs, ZnCdSe/ZnS QDs and CsPbBr₃@Biotin probes were calculated in the same way.

3. Measurement of photoluminescence quantum yield (PL QY)

To calculate the PL QY of CsPbBr₃ NCs, 2,7-dichlorofluorescein (F-27) was used as the reference dye. As we know, the QY of F-27 is 87% under 465 nm excitation. Thus, the absorbance of both CsPbBr₃ NCs and F-27 at 465 nm was recorded by an absorption spectrometer. Then, the PL spectra of CsPbBr₃ NCs and F-27 were measured by using 465 nm excitation. After the integral area of PL spectra were calculated, the QY of CsPbBr₃ NCs was obtained by the following classical equation (1):

$$Q = Q_R \cdot \frac{I}{I_R} \cdot \frac{OD_R}{OD} \cdot \frac{n^2}{n_R^2}$$
(1)

where Q is QY, I is the integral area of PL spectra, OD is optical density at the excitation wavelength and n is the refractive index of the solvent. "R" in lower case stands for the reference dye. The data of three independent measurements were shown in Table S1. The solvent of F-27 is 0.1 M NaOH (n_R =1.335), and the solvent of CsPbBr₃ NCs is water (n=1.333). As a result, the PL QY of CsPbBr₃ NCs were 70.4%.

F-27		CsPbBr ₃ NCs	
Absorbance (OD_R)	Integral area (I_R)	Absorbance (<i>OD</i>)	Integral area (1)
0.0099	17647.32	0.0125	17867.25
0.0204	24160.65	0.0207	19658.41
0.0306	32335.98	0.0322	28263.52

Table S1. The absorbance and PL integral area of CsPbBr₃ NCs and F-27.



Figure S1. (a) The on-off duty cycle values of CsPbBr₃ NCs plotted versus time. (b) Enlarged region as indicated by the purple box in (a).



Figure S2. Characterization of CdSSe@ZnS QDs. (a) TEM images of CdSSe@ZnS QDs. The scale bar is 20 nm. (b) Absorption and (c) emission spectra of CdSSe@ZnS QDs. (d-e) Single-particle luminescence microscopic images of CdSSe@ZnS QDs: (d) wide field image (green), (e) SMLM image (red), (f) merged image of (d) and (e). The scale bar is 100 nm.



Figure S3. Characterization of ZnCdSe@ZnS QDs. (a) TEM images of ZnCdSe@ZnS QDs. The scale bar is 20 nm. (b) Absorption and emission spectra of ZnCdSe@ZnS QDs. (c) Localization precision of ZnCdSe@ZnS. The excitation light was 488 nm. (d-f) Single-particle luminescence microscopic images of ZnCdSe@ZnS QDs: (d) wide field image (green), (e) SMLM image (red), and (f) merged image of (d) and (e). The scale bar is 100 nm.



Figure S4. (a) The merged image of wide field and SMLM images. (b-f) The cross-sectional profiles along the white lines in the inset images (inset: the enlarge images of dots 1 - 5 in (a). (b) dot 1, (c) dot 2, (d) dot 3, (e) dot 4, and (f) dot 5. All scale bars are 100 nm.). (g-k) Localization precision of (g) dot 1, (h) dot 2, (i) dot 3, (j) dot 4, and (k) dot 5.



Figure S5. (a) The merged image of wide field and SMLM images. (b-j) Localization precision of (b) dot 1, (c) dot 2, (d) dot 3, (e) dot 4, (f) dot 5, (g) dot 6, (h) dot 7, (i) dot 8, and (j) dot 9.



Figure S6. The co-localization results of exosomes labeled with CsPbBr₃ NCs and CM-DiI. (a, b-1) corresponding to Figure 4(c, e-1), respectively; (a, b-2) CM-DiI channel; (a, b-3) the merge channel.



Figure S7. The size distribution of Figure 5b.



Figure S8. (a) The on-off duty cycle values of CsPbBr₃@Biotin plotted versus time. (b) Enlarged region as indicated by the purple box in (a).



Figure S9. Cell membrane of SKBR3 cells labeled with CsPbBr₃@Biotin. The wide-field TIRF image of (a) cell membrane labeled with CsPbBr₃@Biotin, (b) cell nucleus dyed in blue by DAPI and (c) the overlay of (a) and (b). (d) The reconstructed wide-field TIRF image of (a). (e) SMLM image of the same cell. (f) Cross-sectional profiles along the yellow arrows in (d, e). All scale bars are 5 μ m.



Figure S10. NPC channels of HeLa cells labeled with CsPbBr₃@Biotin. The wide-field images of (a) the NPCs channels labeled with CsPbBr₃@Biotin, (b) cell nucleus stained by DAPI and (c) the overlay of (a) and (b). (d) SMLM image of the same cell. (e-f) The cross-sectional profiles along the white lines in the inset images (inset: the enlarged images of circles 1 and 2 in (d). All scale bars are 20 nm).