Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

NIR-driven water splitting formation of layered bismuth oxyhalide materials for effectively photodynamic therapy

Dan Yang, Guixin Yang, Jiaqi Li, Shili Gai, Fei He*, and Piaoping Yang**

Key Laboratory of Superlight Materials and Surface Technology, Ministry of Education, College of Material Sciences and Chemical Engineering, Harbin Engineering University, Harbin, 150001, P. R. China.

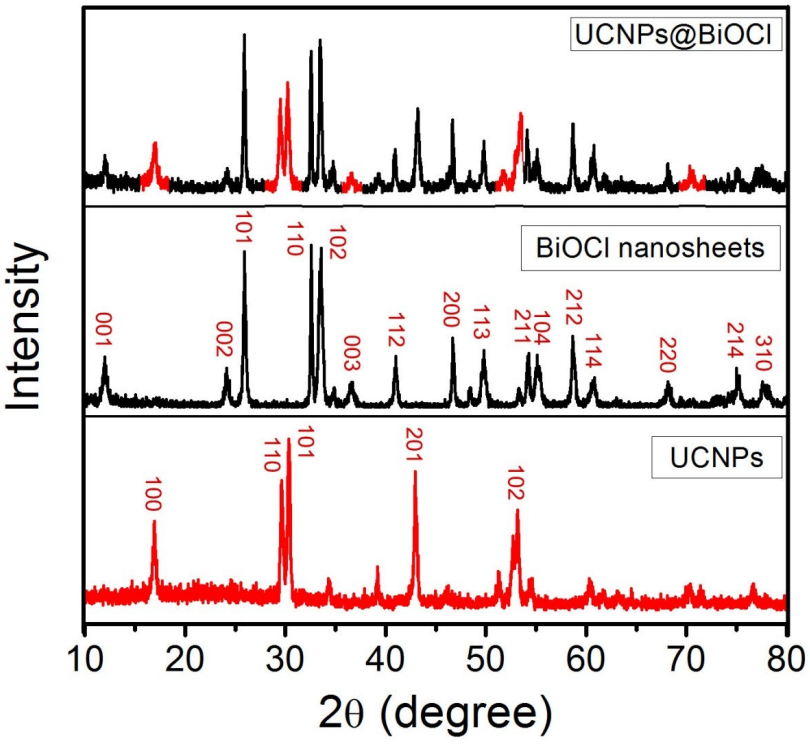

Fig. S1 XRD patterns of as-prepared samples.The corresponding XRD patterns in 2θ range from 10° to 80°.

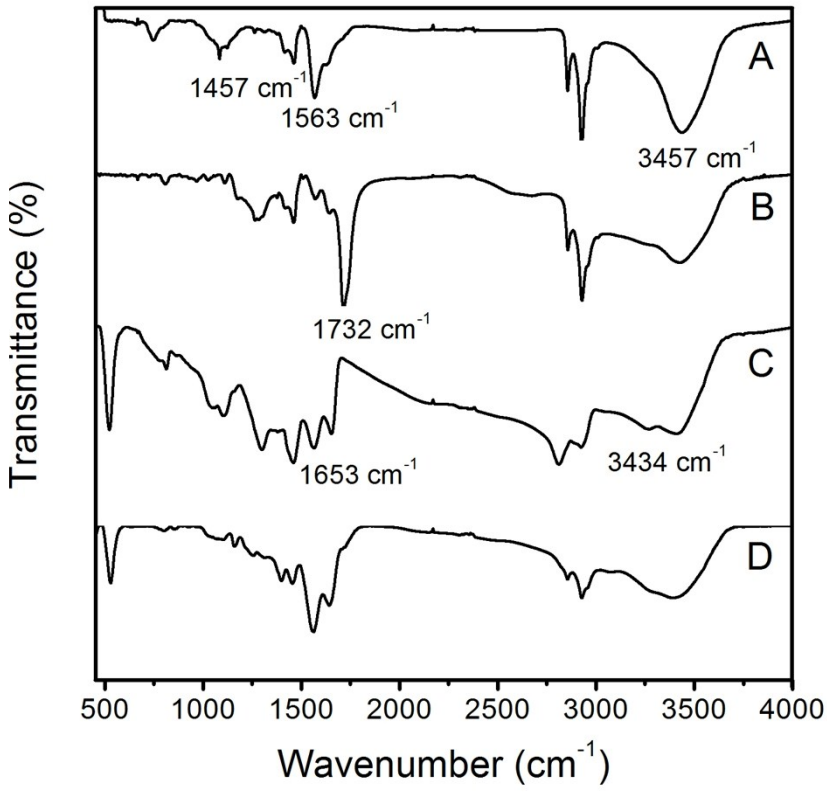

Fig. S2 FT-IR spectra of (A) OA-UCNPs, (B) PAA-UCNPs, (C) PEI-BiOCl and (D) UCNPs@BiOCl.

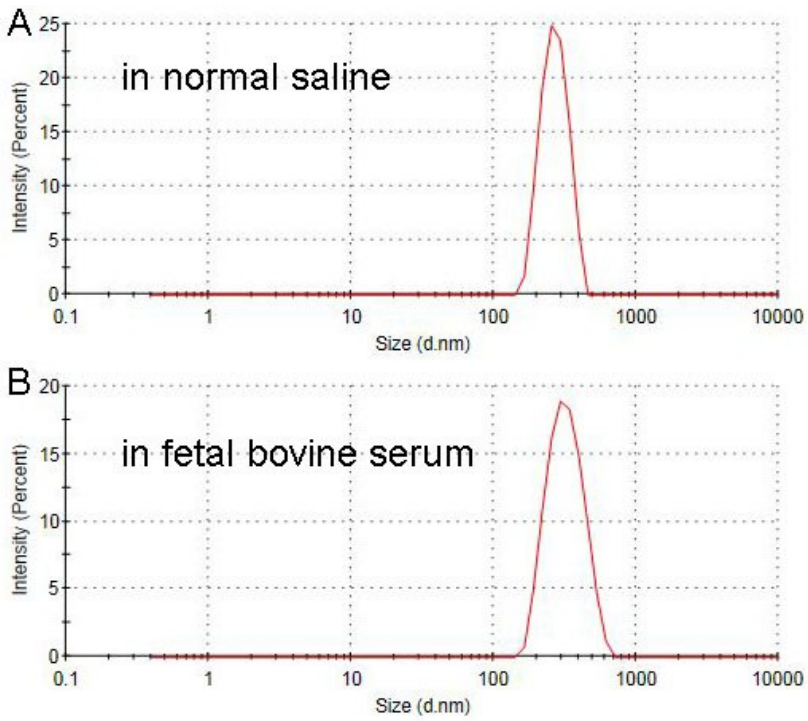

Fig. S3 DLS size distribution of as-made UCNPs@BiOCl in normal saline and fetal bovine serum after 14th days-standing.

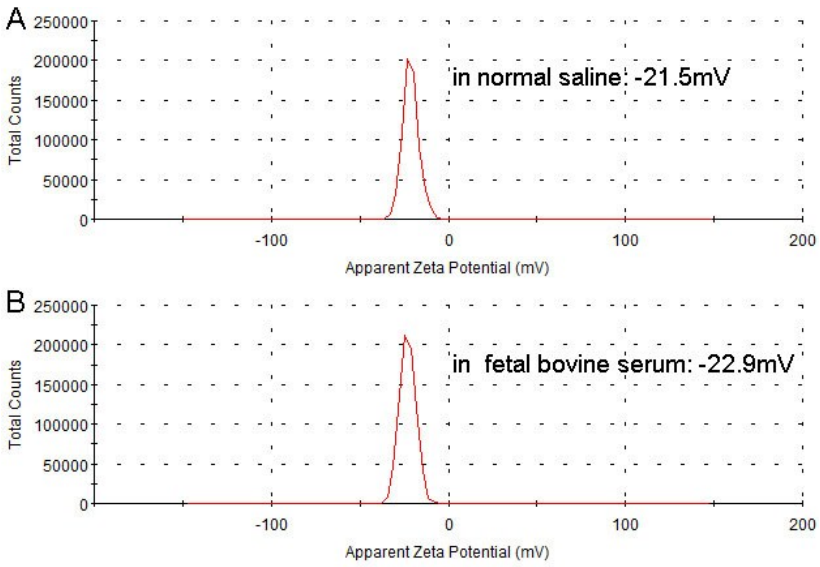

Fig. S4 Zeta potentials of as-made UCNPs@BiOCl in normal saline (A) and fetal bovine serum (B) after 14th days-standing.

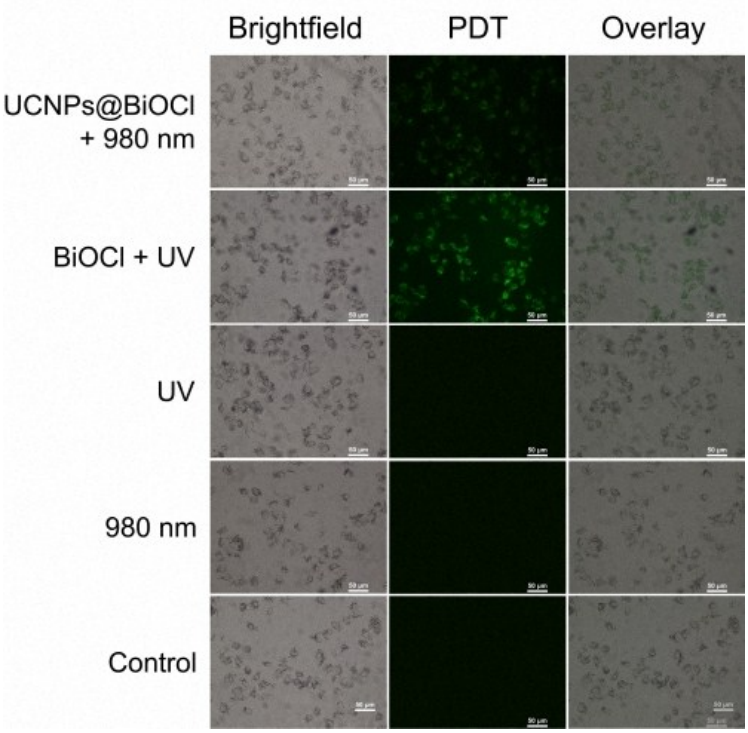

Fig. S5 CLSM bright-field and overlay images of HeLa cells incubated with UCNPs@BiOCl, BiOCl under UV light irradiation, UCNPs@BiOCl under 980 nm laser irradiation, and only the UV and 980nm laser irradiation. All the cells were marked with DCFH-DA.

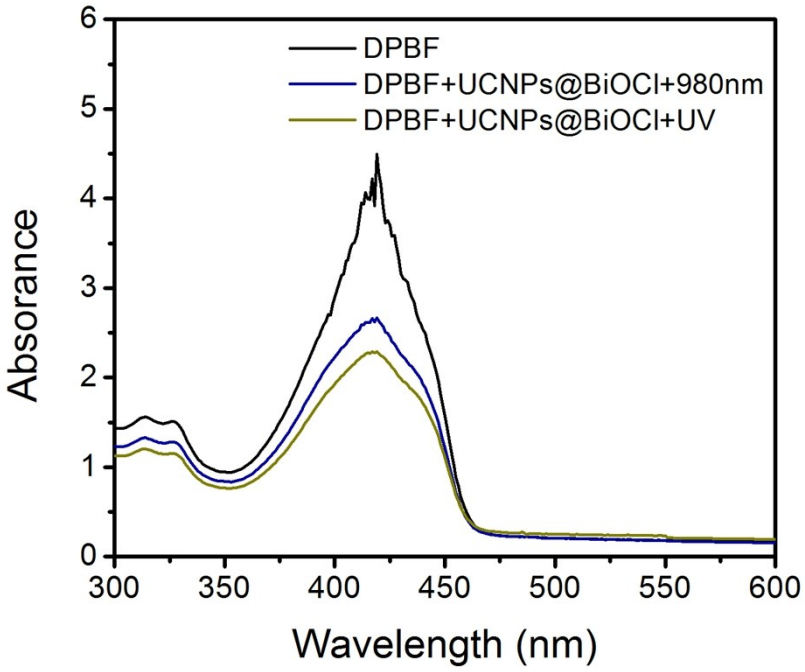

Fig. S6 Absorbance intensity of DPBF mixed with UCNPs@BiOCl excited by 980 nm and UV.

The quantitative comparison of singlet oxygen production efficacy of UCNPs@BiOCl excited by 980 nm and UV were provided in Fig. S6. Based on our experiment condition, DPBF probe was employed to obtain the singlet oxygen production efficacy of UCNPs@BiOCl excited by 980 nm or UV quantitatively. The results indicated that the absorbance intensity of DPBF mixed with UCNPs@BiOCl and excited by UV is slight lower than the group mixed with UCNPs@BiOCl and excited by 980 nm, indicating more reactive oxygen species (ROS) were produced by the former group. Because for the latter group by 980 nm, the used UV/vis lights (which can drive pure water splitting of BiOCl sheets to produce plenty of ROS) was coming from the emissions of UCNPs by 980nm excitation. Therefore, the light conversion process of UCNPs decreases the intensity of produced UV/vis region emission, at the same time, produce less ROS. Fortunately, the use of 980 nm light and UCNPs replace the normal UV/vis light to produce ROS, thus, raise

the tissue penetration of the excitation light, which is very important to realize deep tissue therapy application.

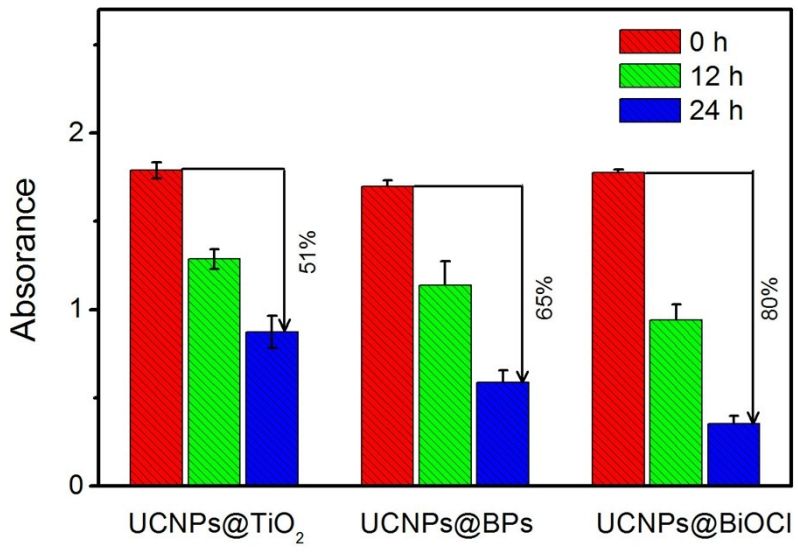

Fig. S7 Absorbance intensity of DPBF mixed with UCNPs@TiO_2, UCNPs@BPs UCNPs@BiOCl at the wavelength of 410 nm under 980 nm laser (0.5 W/cm^2). The recording time is 0, 12 h, and 24 h, respectively.

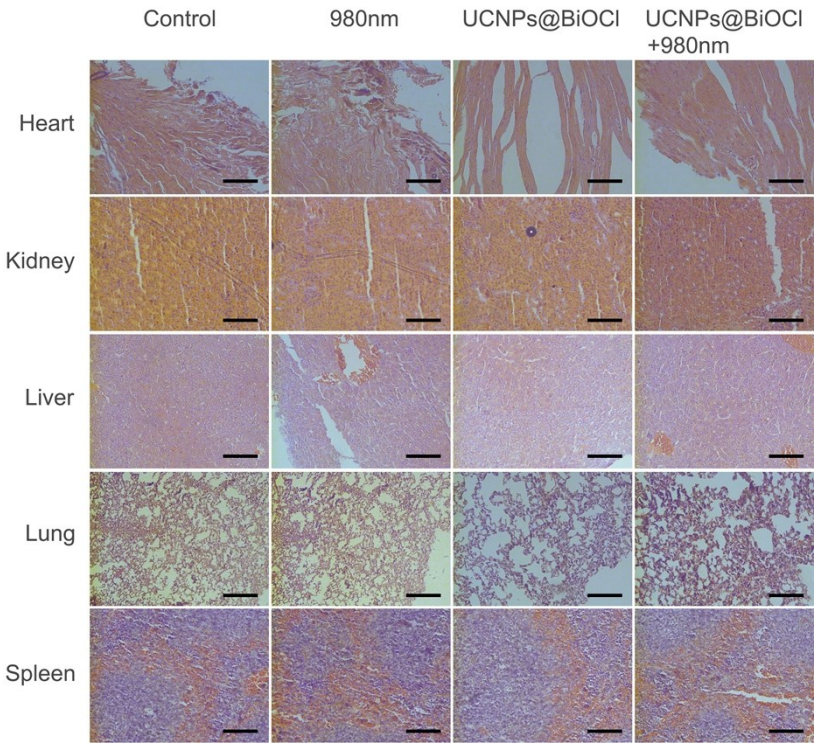

Fig. S8 Representative H&E stained histological images of the superficial regions of heart, liver, spleen, lung and kidney slices. Scale bars for all images are 50 μm.

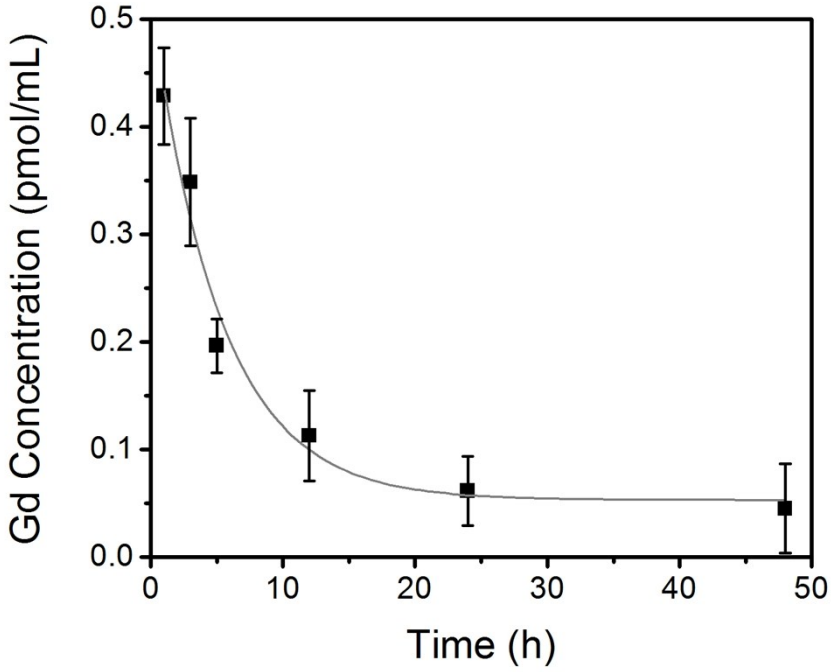

Fig. S9 The Gd concentration in blood at different time after intravenous injection of the UCNPs@BiOCl nanoparticles.

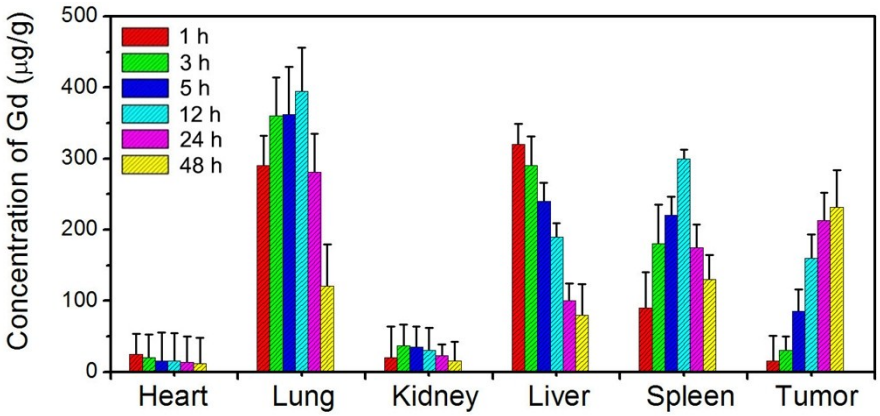

Fig. S10 The bio-distribution of Gd in major organs and tumor of mice after injection of UCNPs@BiOCl intravenously at different time points. Error bars indicate standard deviations, n = 5.

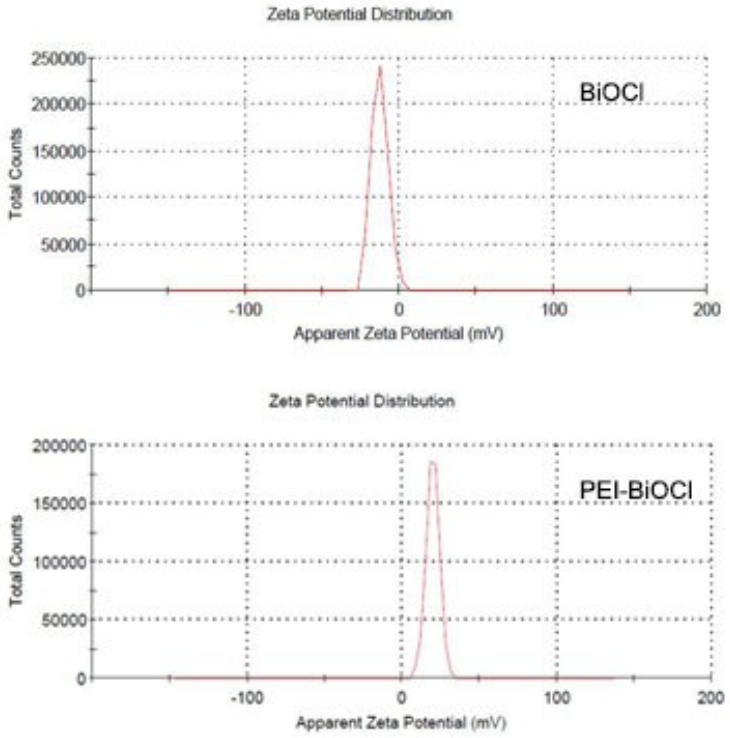

Fig. S11 The zeta potential of BiOCl before and after modified by PEI

The BiOCl nanosheets which has negative charge was integrated with PEI by electrostatic reaction. The zeta-potential results show that BiOCl nanosheets are negatively charged (~ -12.7mV) before PEI modification. Our PEI modification changed BiOCl nanosheets to positively charge (~ 19.8 mV).

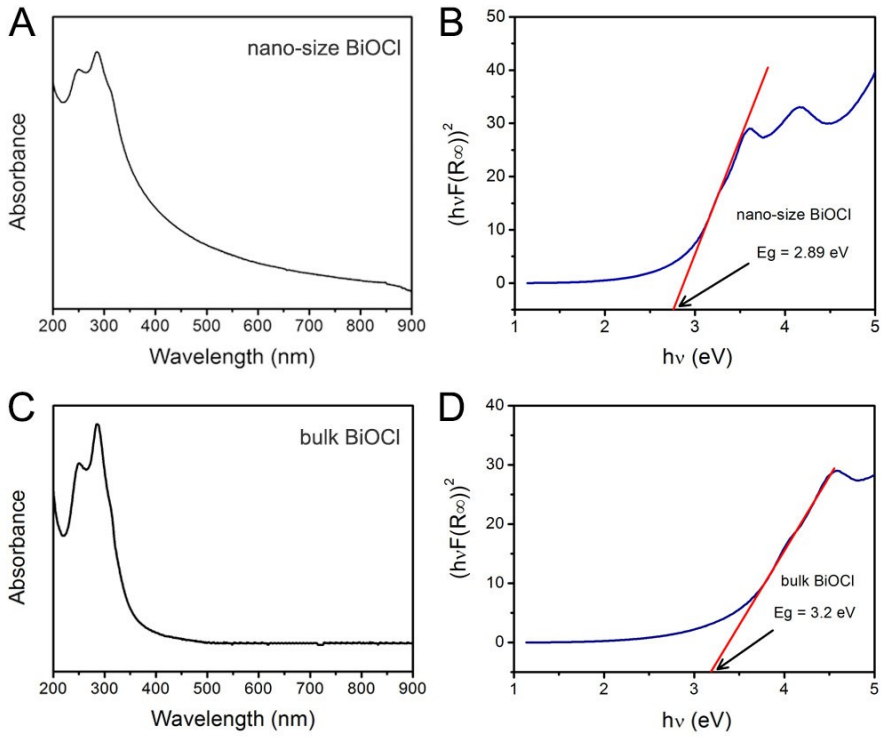

Fig. S12 UV-Vis-NIR absorption spectra and diffuse reflectance spectra of bulk BiOCl, BiOCl nanosheets.

UV-Vis-NIR absorption spectra and diffuse reflectance spectra of bulk BiOCl, BiOCl nanosheets.are showed in Fig.S12. By means of data calculating and fitting, the band-gap of the bulk and nano-size BiOCl are 2.89 eV and 3.2 eV, respectively.

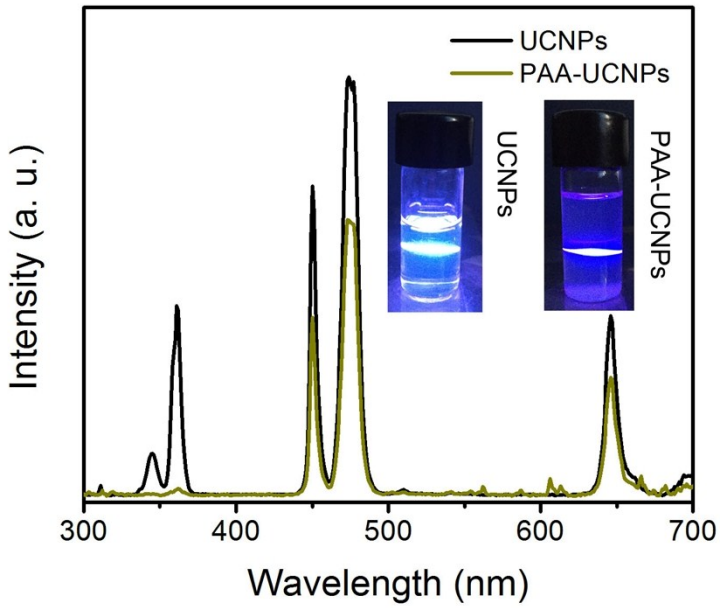

Fig. S13 The UCL spectra and photographs before and after modified by PAA

The UCL spectra and photographs before and after modified by PAA have been presented in Fig. S13. The results show that the upconversion luminescence is mildly quenching due to the modification of PAA.

Table S1 Blood biochemistry and hematology data of female Balb/c mice at 14 days

Project Name	Treatment Group Mean ± SD	Control Group Mean ± SD	units
ALT	45.2 ± 2.7	43.7 ± 7.5	U/L
AST	144 ± 1.5	146.5 ± 4.8	U/L
ALP	170 ± 13	181.6 ± 20.5	U/L
A/G	1.02 ± 0.02	1.04 ± 0.02	
BUN	14.9 ± 0.9	15.1 ± 2.5	mmol/L
WBC	7.1 ± 0.8	8.18 ± 1.1	10^9/L
RBC	7.9 ± 0.5	9.6 ± 0.2	10^{12}/L
HGB	14.3 ± 0.43	15.1 ± 0.85	g/L
PLT	463 ± 43.8	545.8 ± 58.1	10^9/L
HCT	0.52 ± 0.02	0.52 ± 0.04	%
MCV	45.6 ± 1.5	45.8 ± 2.3	fL
MPV	5.3 ± 0.3	5.3 ± 0.5	pg
MCHC	20.4 ± 0.2	19.8 ± 0.9	g/L

Notice: the data in the table is average calculated by five mice each group. Healthy female Balb/c mice i.v. injected with UCNPs@@BiOCl (0.5 mg/mL) were sacrificed at 14 days for blood collection. Serum biochemistry data including blood urea nitrogen (BUN) levels, albumin/globin ratios, and liver function markers: aspartate aminotransferase (AST), alkaline phosphatase (ALP), alanine aminotransferase (ALT), blood urea level (BUN), the ratio of albumin and globulin (A/G), red blood cells (RBC), white blood cells (WBC), mean corpuscular volume (MCV), hemoglobin (HGB), mean corpuscular haemoglobin (MCH), mean corpuscular hemoglobin concentration (MCHC), platelets (PLT), and hematocrit (HCT).