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

Electronic Supporting Information

For

A Dual-Fluorescent Nano-Carrier for Delivering Photoactive Ruthenium Polypyridyl Complex

Content

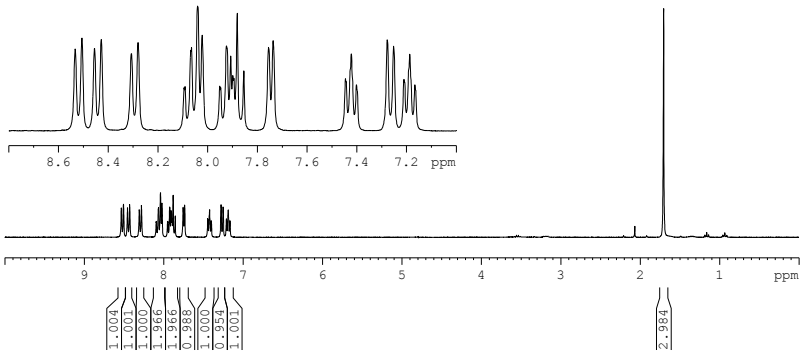

Figure S1. ^{1}H-NMR spectrum of $[Ru(bpy)_2(dmbpy)]Cl_2$ in D_2O. The spectrum was recorded using presaturation pulse sequence to suppress the residual HDO signal. The 1.705 ppm peak of the methyl signal from the 6,6'-dimethyl-2,2'-bipyrdine. All of 11 unique signals from aromatic group were observed in consideration of the symmetry of the complex. (two of which are overlapping).

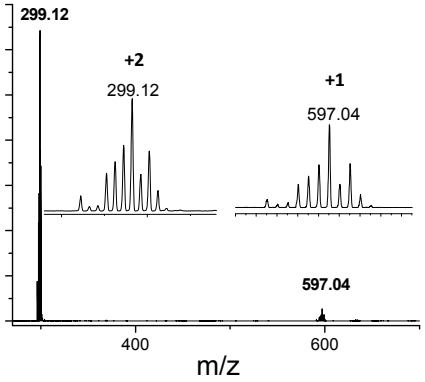

Figure S2. Identification of **Ru-1** by ESI-MS. The spectrum was measured in the positive mode. Composition: $RuC_{32}H_{28}N_6$, measured ESI-MS spectrum: m/z = 597.04, z = 1; m/z = 299.12, z = 2; theoretically calculated isotope pattern, m/z = 596.67, z = 1, m/z = 298.84, z = 2.

Table S1. The size distribution and zeta-potential of free UCNPs, HSA-UCNPs and Ru-HSA-UCNPs.

	Free UCNPs	HSA-UCNPs	Ru-HSA-UCNPs
Size (nm)	60	105	120
PDI	0.16	0.068	0.092
Zeta-potential	+5	-20.3	-45.3

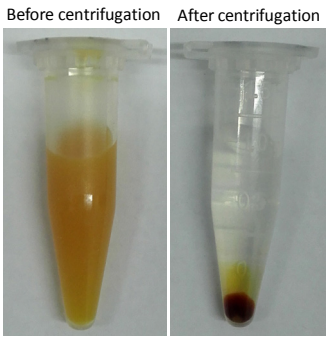

Figure S3. Photos of Ru-HSA-UCNPs before and after centrifugation. The Ru-HSA-UCNPs were dispersed in water showing deep yellow solution. The Ru-1 was completely co-precipitation after 15000 rpm centrifugation for 10 min. The precipitation were resuspended after sonication dispersion.

Table S2. The **Ru-1** loading efficiency measurement.

Amount (μmol)	1	2	3	4
Loading efficiency (%)	76.7	70.7	66.9	56.5

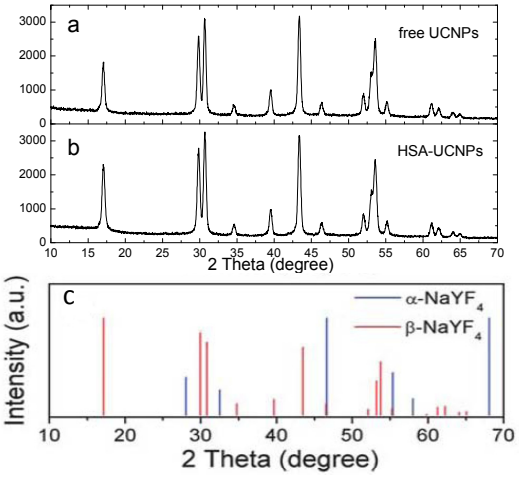

Figure S4. XRD patterns of the $NaYF_4$: 20% Yb, 0.5% Tm nanoparticles. a) free UCNPs. b) HSA-UCNPS. c) the calculated line patterns of α-$NaYF_4$ and β-$NaYF_4$.

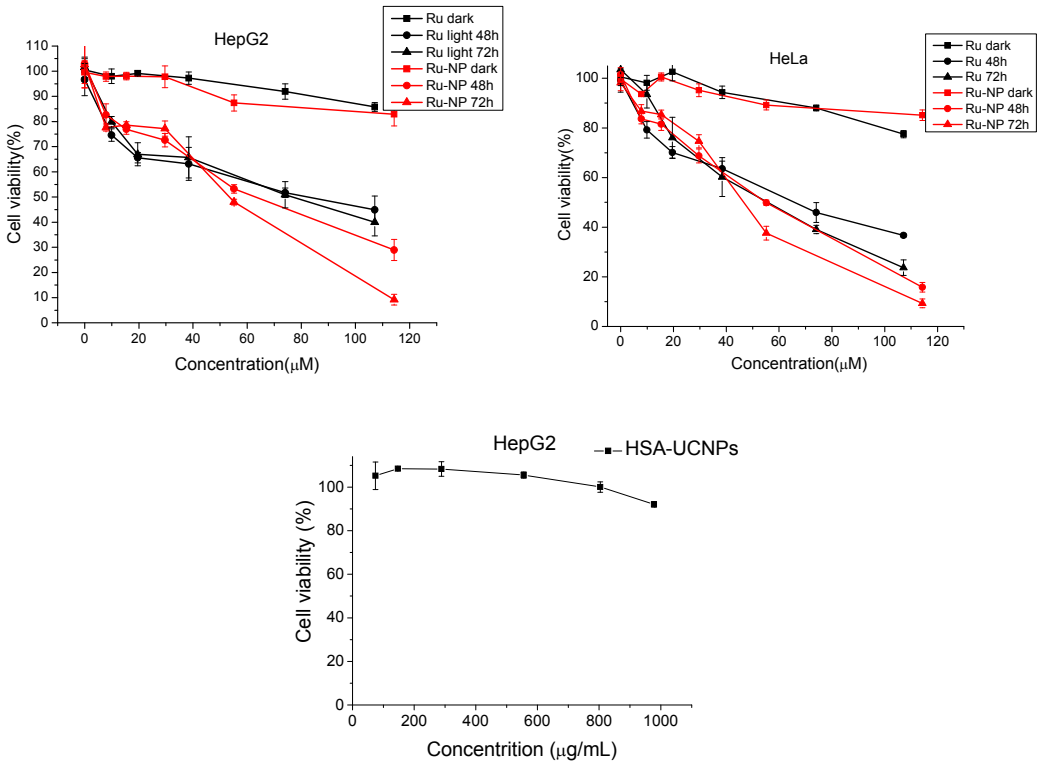

Figure S5. MTT assay of Ru-1, photoactivated Ru-1 on HepG2 and HeLa cells. MTT assay of HSA-UCNPs on HepG2 cells.

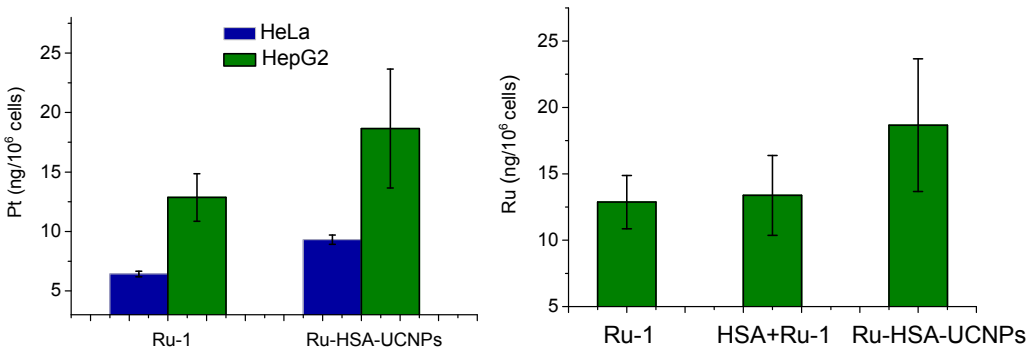

Figure S6. Cellular uptake of ruthenium complexes. (A) The comparison of cellular uptake of **Ru-1** and Ru-HSA-UCNPs on HepG2 cells and HeLa cells. (B) The comparison of cellular uptake of **Ru-1**, HSA + **Ru-1**, Ru-HSA-UCNPs on HepG2 cells. Cells were treated with same ruthenium concentration of 100 μM for 4 hours. The accumulation of ruthenium in cells was measured by ICP-MS.

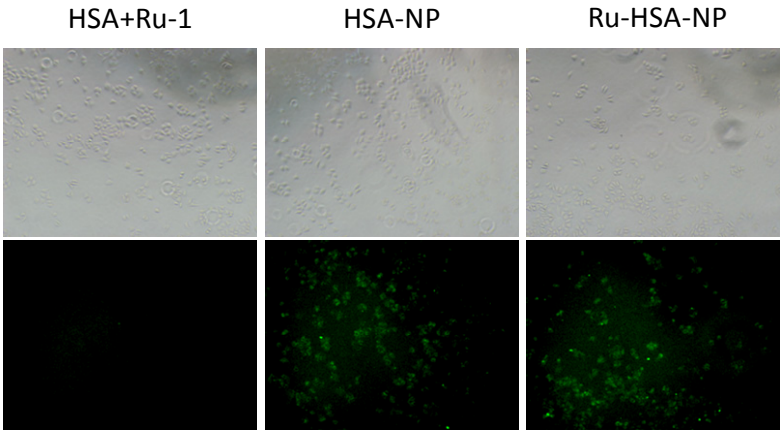

Figure S7. The cellular uptake of HSA and nanoparticles. The cells were treated with HSA protein + **Ru-1**, polymerized HSA nanoparticles (HSA-NP), and **Ru-1** loaded HSA-NP (Ru-HSA-NP) for 4 h on HepG2 cells. The fluorescence images were measured by fluorescence microscopy.

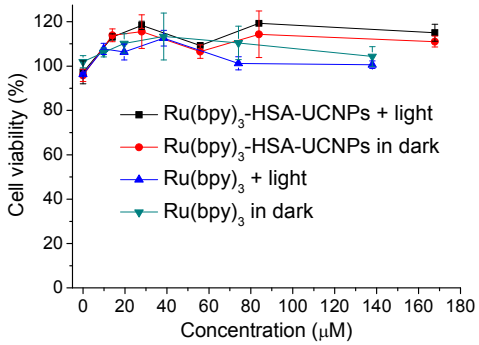

Figure S8. Cytotoxicity assay of free $[Ru(bpy)_3]^{2+}$ and its conjugates of HSA-UCNPs ($Ru(bpy)_3$-HSA-UCNPs). The cell viability was measured on HepG2 cells with the treatment of ruthenium compounds with light irradiation (in 10 mW cm^{-2} irradiation power density) for 10 min or in dark.

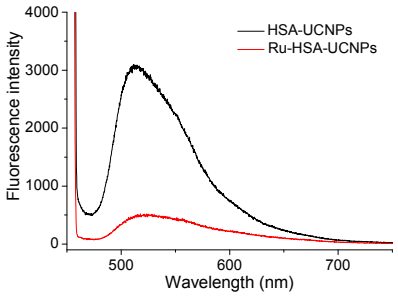

Figure S9. The fluorescence emission spectra of HSA-UCNPs and Ru-HSA-UCNPs. The fluorescence spectra were measured at 450 nm excitation.