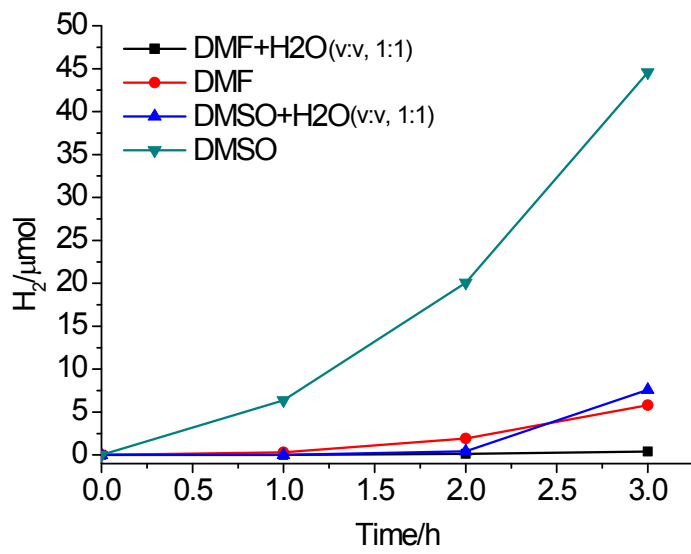


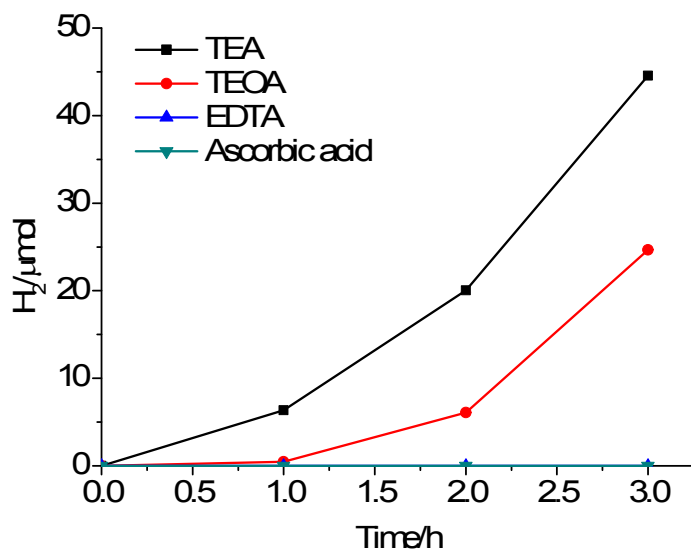
	$E_{1/2}(ox) / V \text{ vs. } Fc/Fc^+$	$E_p(red) / V \text{ vs. } Fc/Fc^+$
Ru2(1)	0.307, 0.600	-1.949 <sup>b</sup> , -2.248 <sup>b</sup>
Ru2(2)	0.302, 0.597	-1.958, -2.28, -2.492
RuIr(1)	0.321, 0.676	-1.951 <sup>b</sup> , -2.215 <sup>b</sup>
RuIr(2)	0.300, 0.532	-1.934, -2.060, -2.310, -2.490
$L_{Ru1}$	0.654 (2nd: 0.346 <sup>a</sup> , 0.594)	-1.952 <sup>b</sup> , -2.224 (2nd: -1.951 <sup>b</sup> , -2.232)
$L_{Ru2}$	0.680 (2nd: 0.318 <sup>a</sup> , 0.685)	-1.932, -2.238 (2nd: -1.928, -2.364)
$L_{Ir}$	0.742 (2nd: 0.738)	-2.014, -2.394 (2nd: -2.082)

a:  $E_p(ox)$ , b:  $E_{1/2}(red)$ .

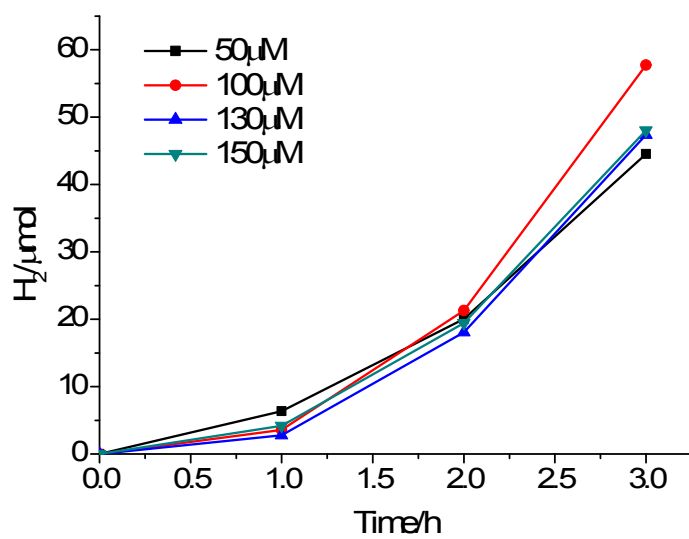
Fig. S1 CV curves and structures of mononuclear Ru(II)/Ir(III) compounds (DMF,  $1 \times 10^{-5} \text{ mol L}^{-1}$ ), and detailed redox potentials of the binuclear and mononuclear compounds.



a)



b)



c)

Fig. S2 Photocatalytic H<sub>2</sub> production results of IrRu(1) as PS under different conditions, (a) different solvents (PS, 50 μM; WRC, 1mg; SR, TEA, 0.72 M), (b) different SRs (PS, 50 μM; WRC, 1mg; solvent, DMSO), (c) different concentrations of PS (WRC, 1mg; SR, TEA, 0.72 M; solvent, DMSO).

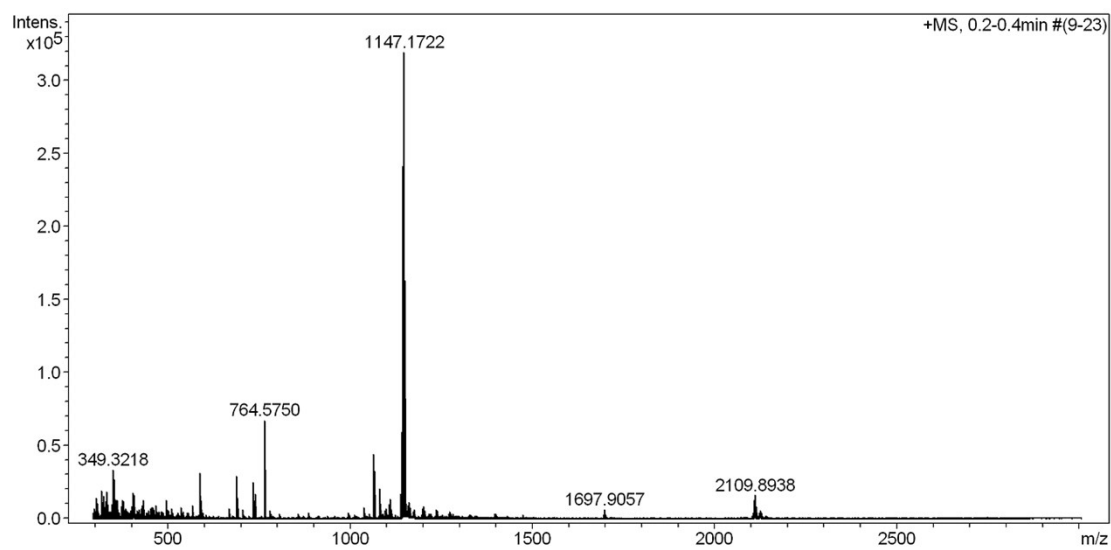
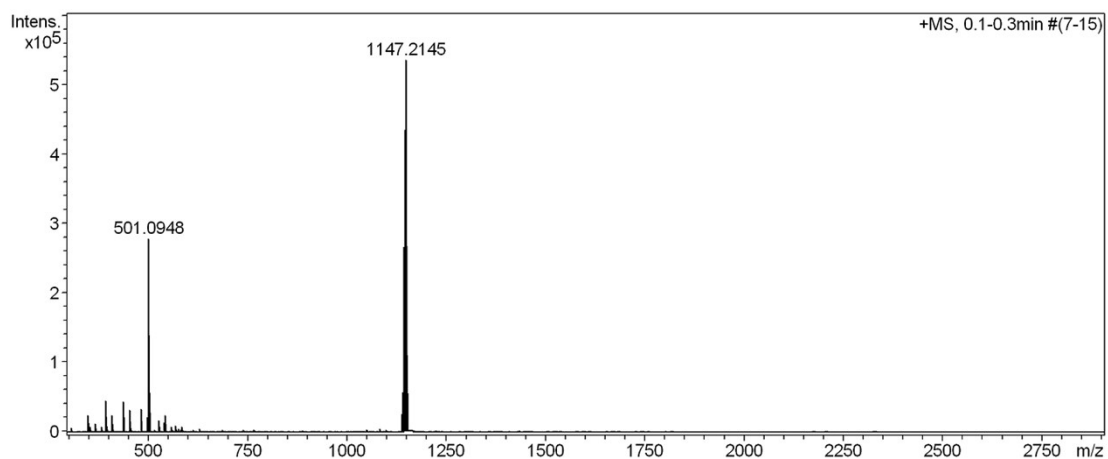


Fig. S3 MS spectra of the photocatalytic system containing IrRu(1) as photosensitizers, showing the persistence of IrRu(1) component in the solution before (top) and after (bottom) photocatalytic process.