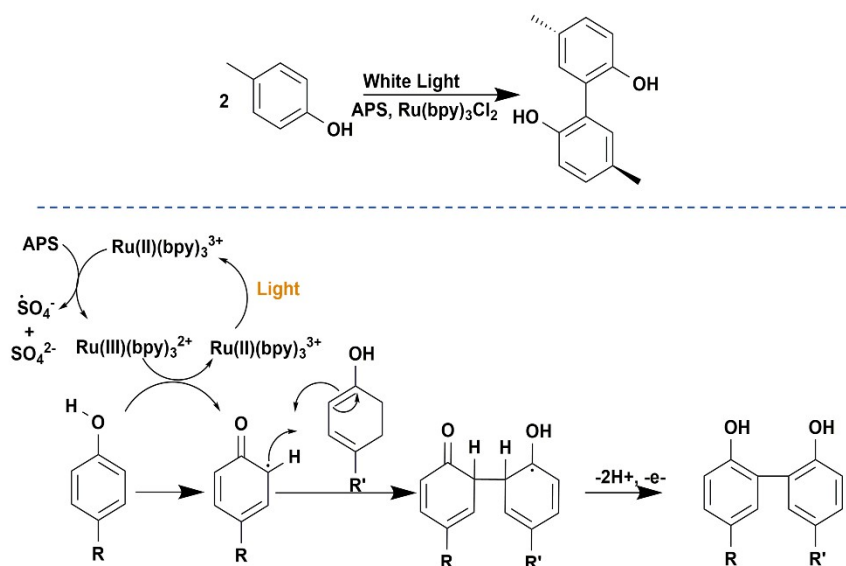
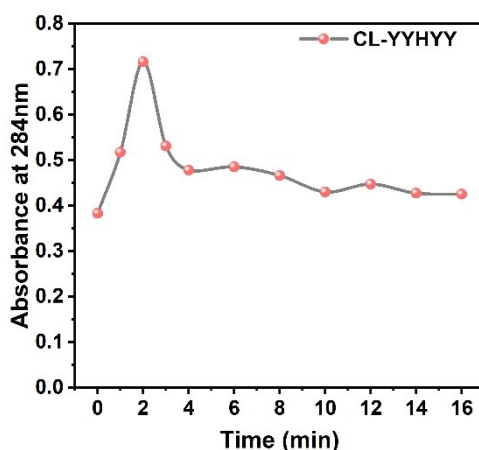


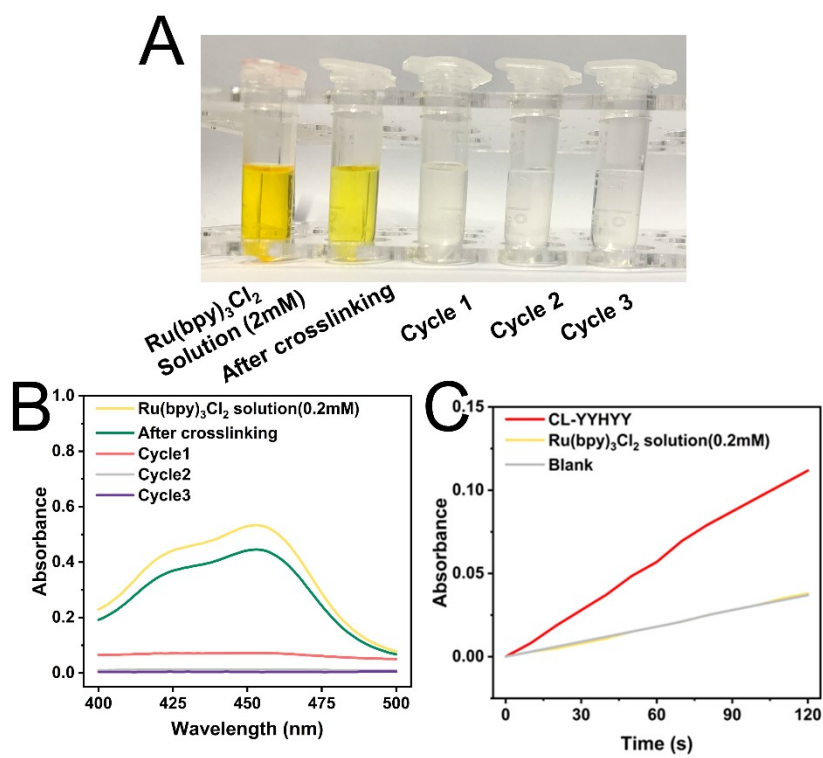
## Supporting Information



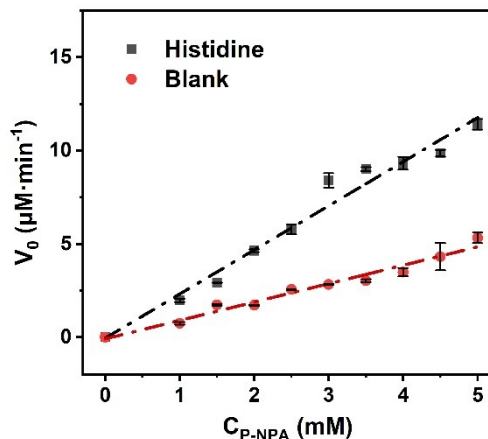
**Fig. S1** Ru-mediated photo-crosslinking of tyrosines triggered by white light. White light activates [Ru(bpy)<sub>3</sub>]<sup>2+</sup> in the presence of the electron acceptor APS. Under the catalysis of [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, electron transfer occurs between tyrosine residues, resulting in the loss of two protons. A covalent bond can be formed between the benzene rings on tyrosine residues, by which the YYHYY peptides can be linked to each other to form crosslinked aggregates of CL-YYHYY.



**Fig. S2** UV absorption at 284 nm during the preparation of CL-YYHYY.



**Fig. S3** (A) The photograph of supernatants after crosslinking reaction and each washing cycle during the preparation of CL-YYHYY. (B) UV-vis spectra of supernatants after each washing cycle. (C) Hydrolysis activity analysis of CL-YYHYY and [Ru(bpy)<sub>3</sub>]<sup>2+</sup>.

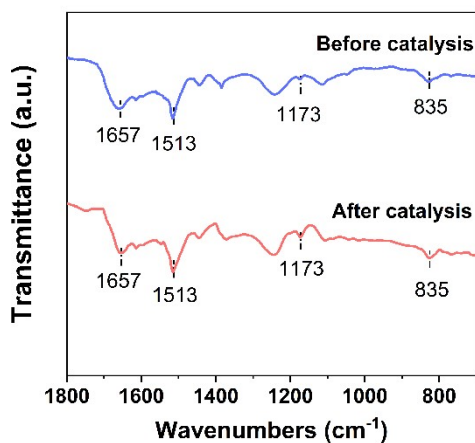


**Fig. S4 (A)** The kinetic plots corresponding to the hydrolysis rate of free histidine at variable substrate concentrations.

The hydrolysis reaction catalysed by free histidine was proved to follow the first-order reaction kinetics. The apparent second-order rate constant  $k_2$  is obtained by the following eq:

$$k_2 = \frac{k_1 - k_w}{[E_0]}$$

where  $k_1$  is the first-order rate constant determined from the diagram of the initial rates ( $V_0$ ) under different concentrations of pNPA.  $k_w$  is the rate constant of hydrolysis reaction in the absence of catalyst.  $[E_0]$  is the concentration of the catalyst.



**Fig. S5** FTIR spectra of CL-YYHYH before and after the catalytic hydrolysis reaction.