

## Supporting Information

### ***In situ* fabrication of multifunctional gold-amino acid superstructures based on self-assembly**

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### **Electronic Supplementary Information**

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## 1. Materials

Ferrocene-carboxylic acid (Fc-COOH, 98% in purity), L-tryptophan methyl ester hydrochloride (98% in purity), O-(1H Benzotriazol-1-yl)-N, N, N', N'-tetramethyluronium tetrafluoroborate (TBTU), and anhydrous CH<sub>2</sub>Cl<sub>2</sub> were purchased from Aladdin (Shanghai, China). All other chemicals with analytical grade were obtained from commercial sources.

## 2. Experimental Section

**Synthesis of Fc-W.** 1) Synthesis of Fc-W-OMe. The reaction was carried out under anhydrous conditions. Ferrocene-carboxylic acid (230 mg, 1 mM) was dissolved in 20 mL CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>3</sub>N (1.5 mL, 10.8 mM) was added to the solution dropwise to activate the carboxyl group, then H-Trp-OMe·HCl (254 mg, 1 mM) and TBTU (353 mg, 1.1 mM) were added to the mixtures. The mixtures were stirred at room temperature for 2 h. After reaction, the solution was extracted with 50 mL 1 M HCl, 50 mL 1 M NaHCO<sub>3</sub>, and 50 mL pure water, respectively. The organic phase was dried with anhydrous sodium sulfate, and the CH<sub>2</sub>Cl<sub>2</sub> was then removed by rotary evaporation at 49 °C. The orange product was used in the next step without any purification. 2) Synthesis of Fc-W. The Fc-W-OMe (1 mM) was dissolved in CH<sub>3</sub>OH (20 mL) and mixed with NaOH aqueous solution (10 mL, 1 M), the reaction mixture was stirred for 2 h. After reaction, the mixture was neutralized by 0.1 M HCl, and the CH<sub>3</sub>OH was then removed by rotary evaporation at 50 °C, resulting in the orange suspension. The suspension was dissolved in CH<sub>2</sub>Cl<sub>2</sub> followed by washing with 50 mL 1 M HCl, 50 mL 1 M NaHCO<sub>3</sub>, and 50 mL pure water, respectively (Fig. S1). The organic phase was dried over anhydrous sodium sulfate, and the CH<sub>2</sub>Cl<sub>2</sub> was then removed by rotary evaporation at 49 °C. The crude product was purified by column chromatography (DCM:MeOH = 20:1, v/v). The prepared Fc-W was further purified by the recrystallization method. Fc-W powder was dissolved in methanol with a saturated concentration, then the solution was added into the ddH<sub>2</sub>O dropwise at 10 °C with continuous stirring. The golden powder was separated out from the water and filtered, and then was freeze-dried. The synthesized Fc-W was analyzed by high performance liquid chromatography (HPLC) (Fig. S2), <sup>1</sup>H nuclear magnetic resonance (NMR) (Fig. S3), <sup>13</sup>C NMR (Fig. S4), high resolution mass spectrometer (HR-MS) (Fig. S5), and elemental analysis. The purity of Fc-W was calculated as >99%. The m/z was measured as 416.08180 g mol<sup>-1</sup>. The elemental analysis was: C<sub>22</sub>H<sub>20</sub>FeN<sub>2</sub>O<sub>3</sub> (416.08): calcd. C 63.48, H 4.84, N 6.73; found. C 63.43, H 4.69, N 6.65.

**Preparation of the Fc-W microflowers.** 1 mg Fc-W powder was dissolved in 1 mL pH 13.0 tris solution, and the formed mixtures were incubated at 25 °C water bath. After self-assembled for 24 h, the floccules were separated from the tubes, and the microflowers were fabricated.

**Preparation of the Au NPs@Fc-W superstructures.** In a typical experiment, the microflowers were prepared as described above. And 2.4 mM HAuCl<sub>4</sub>·3H<sub>2</sub>O was added to the self-assembled Fc-W solution dropwise. After 3 h incubation at 37 °C, 100 r min<sup>-1</sup>, the Au NPs@Fc-W superstructures were achieved.

**Measurement of photothermal property.** In a typical experiment, 1 mL prepared Au NPs@Fc-W superstructures were set at a quartz cell, and the system was irradiated by 808 nm laser with different intensity continuously. The temperature was recorded every 20s. And the thermal infrared photos

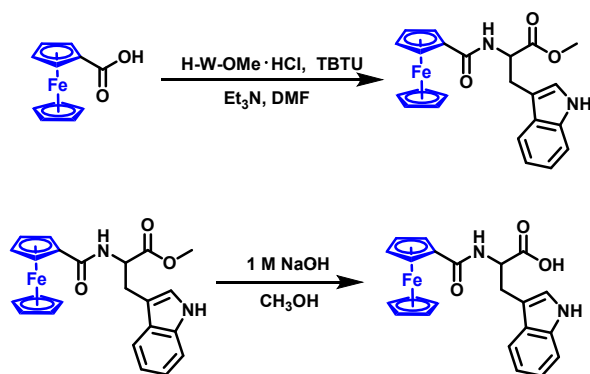
at different temperatures were recorded by infrared camera.

**Catalytic activity.** The catalytic activity of Au NPs@Fc-W superstructures was investigated for the catalytic reduction of 4-NP in the presence of NaBH<sub>4</sub>. In a typical experiment, 4-NP, Au NPs@Fc-W superstructures, and NaBH<sub>4</sub> solution were added **into** the reaction system. The concentration of 4-NP was 0.5 mM and 0.75 mM, the concentration of Au NPs@Fc-W superstructures was 0.24 mM, and the concentration of NaBH<sub>4</sub> solution was 0.3 M. The UV-vis absorption spectra were recorded from 300 nm to 550 nm to monitor the progress of the catalytic reaction.

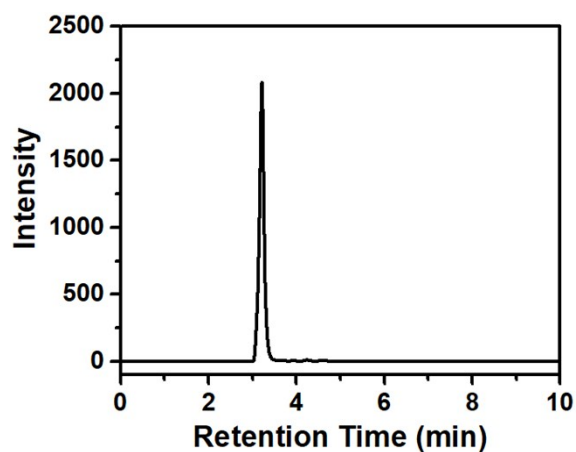
### 3. Characterization

HPLC analysis was taken out on Agilent1100 (Agilent Technologies Inc., USA).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded on the was recorded on Bruker AV-500 spectrometer (Bruker, Germany), referenced to  $\text{Si}(\text{CH}_3)_4$ . The solvent used in the measurement was  $\text{DMSO-d}_6$ . HR-MS was performed on Q Exactive<sup>TM</sup> HF/UltiMate<sup>TM</sup> 3000 RSLCnano (Thermo Fisher, USA) in positive mode. Elemental analysis was performed on the Vairo EL elemental (Elementar, Gemany). SEM images were recorded using an S-4800 field emission SEM (Hitachi High-technologies CO., Japan) at an acceleration voltage of 3 keV, with sputter-coating with platinum using an E1045 Pt-coater (Hitachi High-technologies CO., Japan). TEM analysis was performed on a transmission electron microscope (JEM-2100F, JEOL, Japan) at an accelerating voltage of 120 kV. Elemental analysis was conducted with an energy dispersive X-ray spectrometer (EDS) equipped with SEM. FTIR was recorded on a Nicolet-560 FTIR spectrometer (Nicolet Co., USA) with a KBr pellet method across the range of 400-4000  $\text{cm}^{-1}$ . Powder XRD analysis was obtained using a PANalytical X'Pert PRO MPD system (Panalytical, Netherlands) with  $\text{Cu/K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the  $2\theta$  range of  $5^\circ$ - $50^\circ$ . *In situ* X-ray scattering measurements were carried out at beamline 1W2A of the Beijing Synchrotron Radiation Facility (Beijing, China). The wavelength of the radiation source was  $\lambda = 0.154 \text{ nm}$ . Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed by TGA/DSC1 (Mettler Toledo, Switzerland), under the protection of a nitrogen atmosphere. UV-Vis spectroscopy was analyzed on a TU-1810 UV/vis spectrophotometer (Shanghai Metash Instruments, China) using a 1 mm path length quartz cuvette.

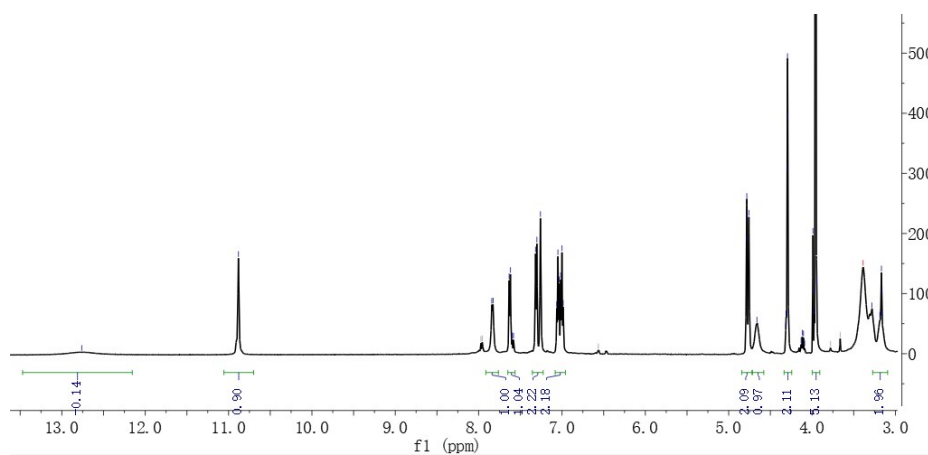
## 4. Supplementary Figures



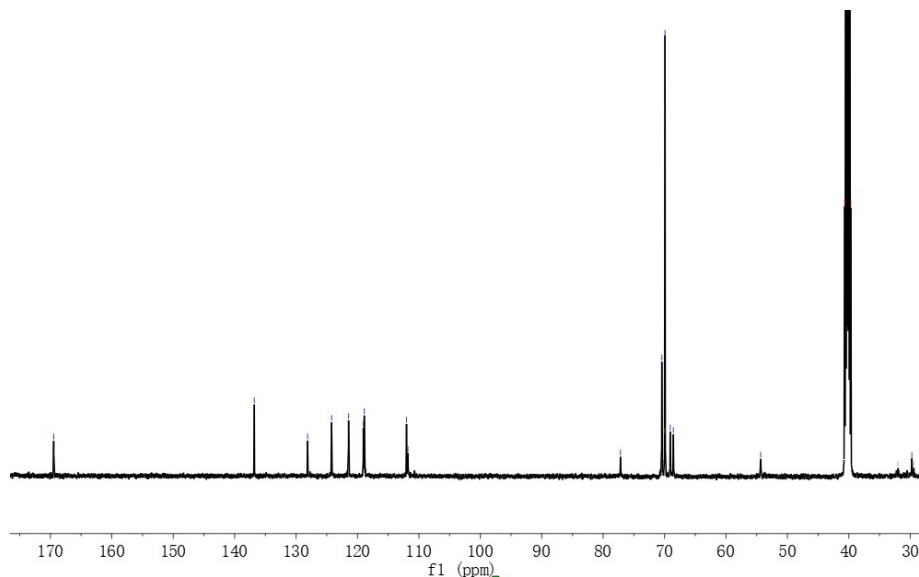
**Fig. S1** The synthetic route of ferrocene- tryptophan (Fc-W).



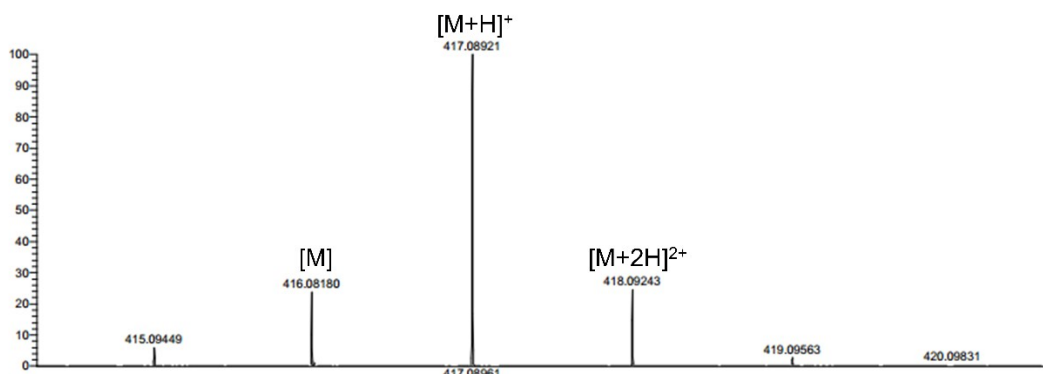
**Fig. S2** HPLC analysis of the synthetic Fc-W. The retention time of Fc-W was 3.2 min with a purity of >99%. The 5.0 mg purified Fc-W was dissolved in 1 mL methanol at a concentration of 5.0 mg mL<sup>-1</sup>. HPLC was carried out using a C-18 column and CH<sub>3</sub>OH-H<sub>2</sub>O (1:1, v/v) as the mobile phase.



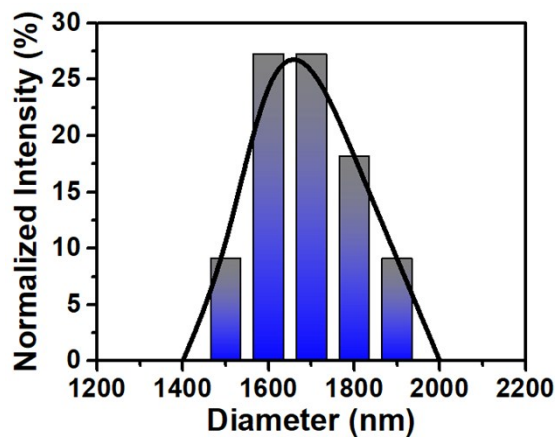
**Fig. S3**  $^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ ) spectra of the synthetic Fc-W: 12.75 (COOH), 10.88 (s, 1H, NH), 7.83 (m, 1H, CH), 7.62 (m, 1H, CH), 7.30 (m, 2H, CH), 7.03 (m, 2H, CH), 4.78 (m, 2H,  $\beta\text{-C}_5\text{H}_4$ ), 4.66 (br, 1H, NH), 4.29 (m, 2H,  $\beta\text{-C}_5\text{H}_4$ ), 3.93 (s, 5H, Cp), 3.17 (m, 2H,  $\text{CH}_2$ ).



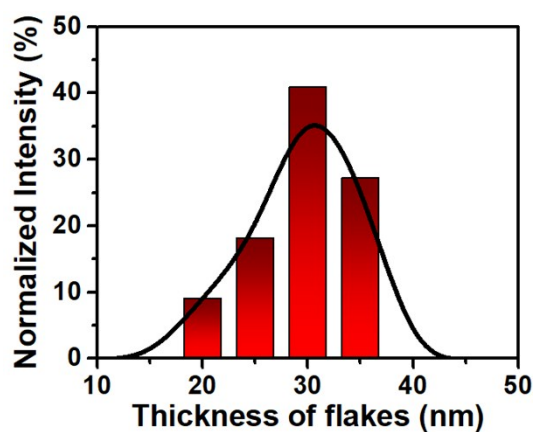
**Fig. S4**  $^{13}\text{C-NMR}$  ( $\text{DMSO-d}_6$ ) spectra of the synthetic Fc-W: 170.45 (C=O), 136.80 (C), 128.12 (C), 124.21 (CH), 121.45 (CH), 119.03 (CH), 118.89 (CH), 112.01 (CH), 111.79 (C), 77.18 ( $\text{C}_{\text{ipso}}$ ), 70.45, 69.97, 69.08, 68.57 ( $\text{C}_5\text{H}_4$ ), 69.92 ( $\text{C}_p$ ), 54.35 (CH), 29.74 ( $\text{CH}_2$ ).



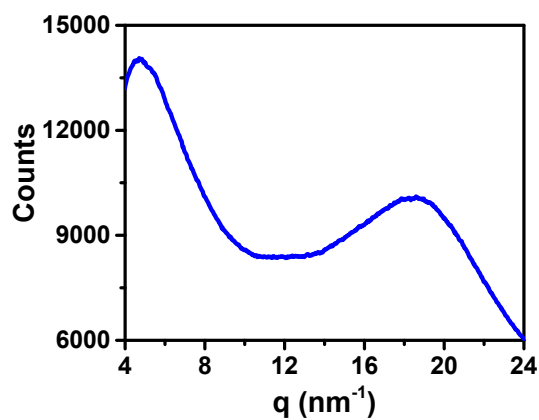
**Fig. S5** HR-MS spectrum of Fc-W, the molecular weight was measured as  $416.08180 \text{ g mol}^{-1}$ .



**Fig. S6** Size distribution of self-assembled Fc-W microflowers, the average diameter was 1.65  $\mu\text{m}$ .



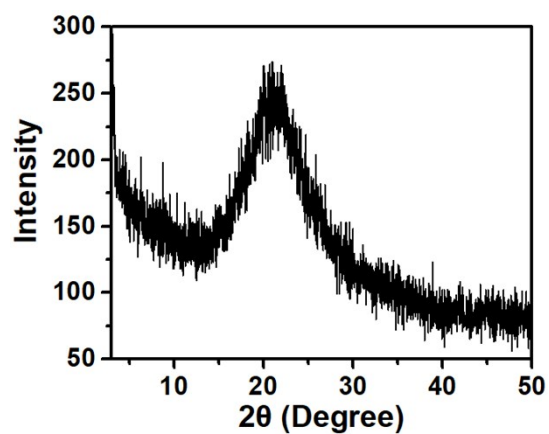
**Fig. S7** Size distribution of the thickness of flakes in the self-assembled Fc-W microflowers, the average thickness was 30.64 nm.



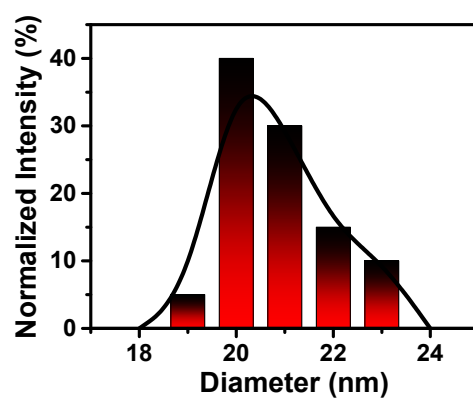
**Fig. S8** 1D profile of *in situ* synchrotron wide angle X-ray diffraction (WAXD) of self-assembled



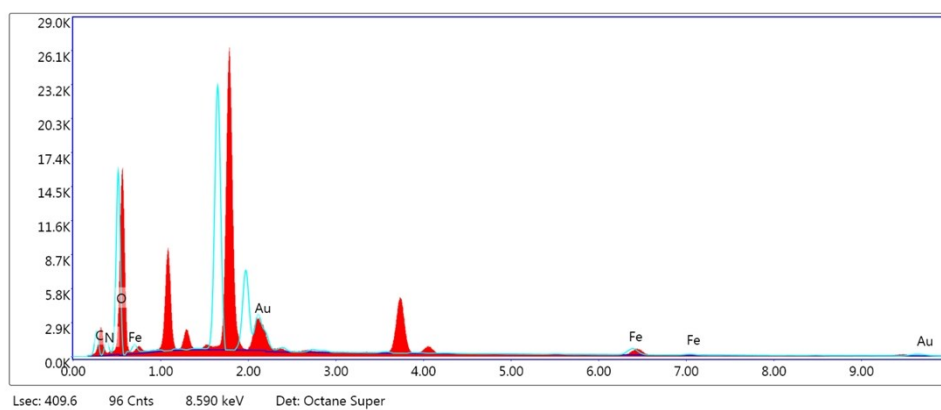
microflowers.



**Fig. S9** Powder X-ray diffraction (XRD) curve of the Fc-W microflowers.

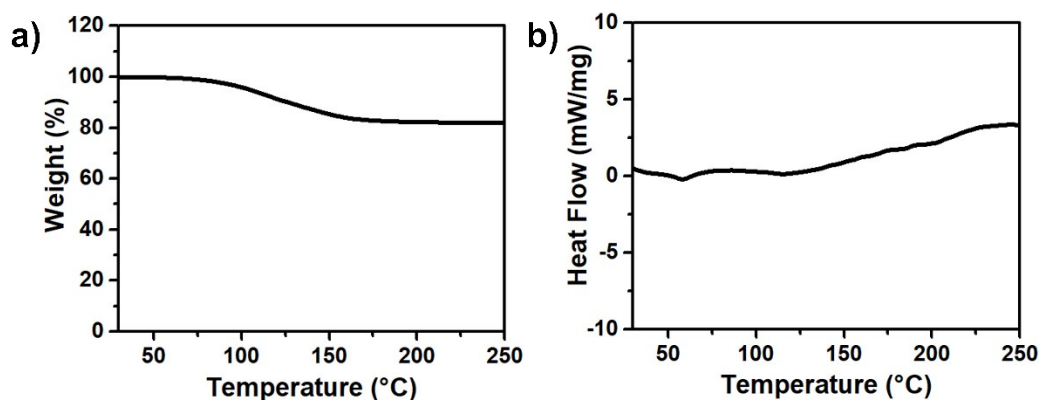


**Fig. S10** The measured size distribution of Au nanoparticles of Au NPs@Fc-W superstructures.

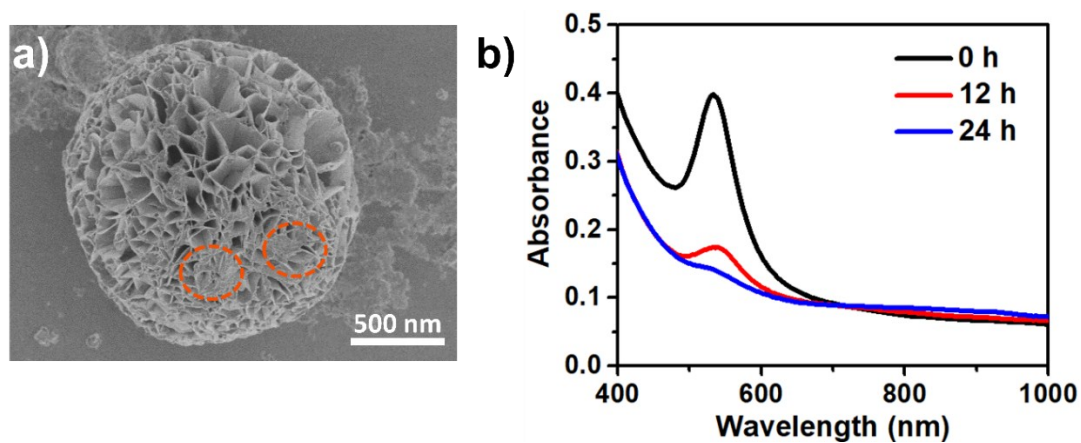


**Fig. S11** Micro-area elemental analysis by energy dispersive spectroscopy (EDS) of the Au

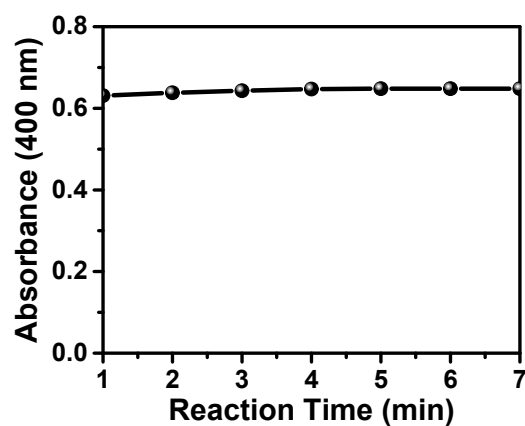
NPs@Fc-W superstructures.



**Fig. S12** TGA and DSC thermograms of Au NPs@Fc-W superstructures.



**Fig. S13** a) SEM image of Au NPs@Fc-W superstructures after incubating for 24 h. b) UV-vis spectrum of Au NPs@Fc-W superstructures at different incubation time.



**Fig. S14** Time-dependent evolution of absorbance at 400 nm at different reaction time catalyzed by Fc-W microflowers.