Electronic Supplementary Information

Protein-assisted synthesis of nanoscale covalent organic frameworks for phototherapy of cancer

Tingting Sun, Rui Xia, Junli Zhou, Xiaohua Zheng, Shi Liu* and Zhigang Xie*

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China.

E-mail: liushi@ciac.ac.cn; xiez@ciac.ac.cn

Contents:

Materials and characterization

Supporting Figures

Scheme S1 The Synthetic route of TAPP.

Scheme S2 The Synthetic route of TFP.

Fig. S1 TEM images of COFs with different feed ratios of BSA: (a) 0 wt%; (b) 21 wt%; (c) 34 wt%; (d) 51 wt%.

Fig. S2 TEM images of COFs obtained by replacing (a) BSA with OVA or (b) TFP with terephthalaldehyde.

Fig. S3 FTIR spectra of TAPP, TFP, BSA and COF-B.

Fig. S4¹³C CP-MAS solid-state NMR spectrum of COF-B.

Fig. S5 (a) Photos of COF-0 (0) and COF-B (1) after storage in water for 0, 1 and 4 days. (b) TEM image of COF-B after storage in water for 4 months.

Fig. S6 Zeta potential of COF-0 and COF-B.

Fig. S7 Linear plot of the cooling time versus $-Ln\theta$ calculated from the cooling stage.

Fig. S8 CLSM images of HeLa cells incubated with COF-B at 37°C for 0.5 and 2 h.

Fig. S9 Viabilities of HeLa cells treated with COF-B without or with 685 nm laser irradiation under different conditions.

Fig. S10 Changes in body weight of mice with tumors after various treatments.

Fig. S11 H&E staining of main organs (heart, liver, spleen, lung, and kidney) after various treatments for 12 days.

Materials and characterization

BSA was purchased from Beijing Solarbio Science & Technology Co., Ltd. Hoechst 33258 and cell viability (live-dead cell staining) assay kit were purchased from Jiangsu KeyGEN Biotechnology Co., Ltd. 0.25% Trypsin-EDTA, Phenol Red(modified) was purchased from Dalian Meilun Biotechnology Co., Ltd. Reactive Oxygen Species Assay Kit (DCFH-DA) was purchased from Shanghai Beyotime Biotechnology Co., Ltd. 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) was purchased from Shanghai yanye Bio-Technology Co., Ltd. The other chemicals were used as obtained commercially.

Analytical balance (XS105DU) and Rainin Pipettes from METTLER TOLEDO were used to quantify solid and liquid respectively. TEM images were taken from JEOL JEM-1011 electron microscope with acceleration voltage of 100 kV. The absorption spectra and FTIR spectra were obtained from UV-2450 UV-vis spectrophotometer (Shimadzu) and Nicolet Impact 410 FTIR spectrometer respectively. ¹³C CP-MAS solid-state NMR spectrum was measured with AVANCE III 400 WB (Bruker). HR-TEM and EDS mapping images were obtained from Tecnai G2 F20 S-TWIN (FEI). The TGA analysis was performed on NetzchSta 449c thermal analyzer system at a rate of 10 °C/min under an air atmosphere. PXRD was performed by a Riguku D/MAX2550 diffractometer. The nitrogen adsorption isotherm was measured on a Micromeritics ASAP 2010 analyzer. CLSM images were obtained from a Zeiss LSM 700 (Zurich, Switzerland).

Supporting Figures



Scheme S1 The Synthetic route of TAPP.



Scheme S2 The Synthetic route of TFP.



Fig. S1 TEM images of COFs with different feed ratios of BSA: (a) 0 wt%; (b) 21 wt%; (c) 34 wt%; (d) 51 wt%.



Fig. S2 TEM images of COFs obtained by replacing (a) BSA with OVA or (b) TFP with terephthalaldehyde.



Fig. S3 FTIR spectra of TAPP, TFP, BSA and COF-B.



Fig. S4 ¹³C CP-MAS solid-state NMR spectrum of COF-B.



Fig. S5 (a) Photos of COF-0 (0) and COF-B (1) after storage in water for 0, 1 and 4 days. (b) TEM image of COF-B after storage in water for 4 months.



Fig. S6 Zeta potential of COF-0 and COF-B.



Fig. S7 Linear plot of the cooling time versus $-Ln\theta$ calculated from the cooling stage.



Fig. S8 CLSM images of HeLa cells incubated with COF-B at 37°C for 0.5 and 2 h.



Fig. S9 Viabilities of HeLa cells treated with COF-B without or with 685 nm laser irradiation under different conditions.



Fig. S10 Changes in body weight of mice with tumors after various treatments.



Fig. S11 H&E staining of main organs (heart, liver, spleen, lung, and kidney) after various treatments for 12 days.