$CuCl_2$ loaded covalent organic framework membrane with a long degree of conjugation for iodine adsorption to achieve sustained antibacterial activity

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Supporting Information

1. Experimental Section

1.1 Chemicals

Iodine and p-toluenesulfonic acid monohydrate (PTSA·H_2O) were purchased from Sigma-Aldrich. 1,3,5-triformylphoroglucinol (Tp), p-phenylenediamine (Pa), 4,4'-diaminodiphenyl (Bd), 4,4"-diaminoterphenyl (Td) were purchased from Yanshen Technology Co., Ltd. Tetrahydrofuran (THF), ethanol and from Sinopharm Chemical Reagent Co., Ltd. Luria Broth (LB) base and agar were purchased from Qingdao Haibo Biotechnology Co. Ltd. All reagents were used without further purification. Water with resistivity of 18 MΩ·cm^{-1} was prepared using a Millipore Milli-Q system and used in all experiments. Escherichia coli (*E. coli*) and Staphylococcus aureus (*S. aureus*) were purchased from Beijing Beina Chuanglian Biotechnology Institute.

1.2 Experimental procedure

1.2.1 Preparation of COF-$CuCl_2$ membranes by screen-printing technique assisted by mechanical grinding method

TpPa-$CuCl_2$, TpBD-$CuCl_2$, and TpTD-$CuCl_2$ COF membranes were prepared in a similar way as reported in the literature [1,2]. 0.3 mmol Pa (or Bd, Td), 0.2 mmol Tp, PTSA·H_2O with 200 μL of 0.3 mmol $CuCl_2·2H_2O$ were ground into a homogeneous gelatinous precursor using a mortar and pestle, which was spread on a 100-mesh screen. The precursor on the screen was scraped onto the glass substrate with a rubber spatula to form a uniform membrane. The film-carrying glass sheet was placed in a tube furnace, inerted with nitrogen and water vapour, and heated in a programmed manner (50 ℃ for 6 h, 90 ℃ for 6 h, 120 ℃ for 12 h, with a rate of increase of 1 ℃/min for each temperature gradient). At the end of heating, the membrane was cooled naturally, and then the glass sheet was put into water, and the membrane was automatically detached from the glass sheet carrier to obtain self-supported TpPa-$CuCl_2$, TpBd-$CuCl_2$ and TpTd-$CuCl_2$ membranes. The above free-standing membranes were repeatedly soaked in H_2O, THF and CH_3CH_2OH for 3 times (12 h each time) to remove the unreacted monomer, catalyst and oligomer. Finally, the membranes were heated in a vacuum oven at 80 ℃ for 24 h to remove the solvent from the membranes.

1.2.2 Study of iodine absorption properties of COF-$CuCl_2$ in I_2/KI aqueous solutions

Testing of the standard curve of aqueous I_2/KI solutions: different concentrations of I_2/KI aqueous solutions were prepared (0.01 mg/mL, 0.02 mg/mL, 0.025 mg/mL, 0.04 mg/mL, 0.05 mg/mL, 0.06 mg/mL and 0.08 mg/mL), and then the absorption values of the above aqueous solutions were tested by UV-vis absorption spectrum. The absorption peaks of I_2/KI aqueous solution at 288 nm and 350 nm are the characteristic peaks of I_3^-. The absorption values at 350 nm were fitted against the concentrations of I_2 in the I_2/KI solutions to obtain the standard equation y= 22.8647x-0.1805, where x is the concentration of I_2 and y is the absorption values. According to the above equation, the concentration of I_2 in the solution changes with time during the adsorption process can be obtained.

The amount of iodine adsorbed by the COF-$CuCl_2$ membrane with respect to adsorbent mass (q_t, mg/g) and the amount of iodine adsorbed by the COF-$CuCl_2$ membrane with respect to COF-$CuCl_2$ molar number of unit cell (q_t^{uc}, g/mol) at a given adsorption time (t_a, min) can be calculated according to the Equation (1-2).

$$q_t = ((C_a^0 - C_a^t) \times V_a)/W_{COF} \quad (1)$$

$$q_t^{uc} = ((C_a^0 - C_a^t) \times V_a)/(W_{COF}/M_{COF}) \quad (2)$$

where C_a^0 (mg/L) is the initial concentration of I_2 in the solution; C_a^t (mg/L) is the concentration of I_2 at a given adsorption time after COF-$CuCl_2$ membrane immersed into the solution; V_a is the volume of the I_2/KI solution (10 mL); W_{COF} is the mass of the COF membranes (5 mg); M_{COF} is the molar mass for unit cell.

The adsorption kinetics data measured experimentally are fitted by pseudo-first-order model and pseudo-second-order model, respectively, as described in Equation (3-4).

$$ln(q_e - q_t) = lnq_e - k_1 t_a \quad (3)$$

$$t_a/q_t = 1/k_2(t_a)^2 + t_a/q_e \quad (4)$$

Where k_1 is the rate constant of the pseudo-first-order model; k_2 is The rate constant of the quasi-second-order model.

When the adsorption equilibrium was reached, the adsorption amount of I_2 with respect to the COF-$CuCl_2$ mass (q_e, mg/g) and COF-$CuCl_2$ molar number of unit cell (q_e^{uc}, g/mol) was calculated according to Equations (5-6).

$$q_e = ((C_a^0 - C_a^e) \times V_a)/W_{COF} \quad (5)$$

$$q_e^{uc} = ((C_a^0 - C_a^e) \times V_a)/(W_{COF}/M_{COF}) \quad (6)$$

Where C_a^e is I_2 concentration at equilibrium. To test the maximum adsorption capacity of COF-$CuCl_2$ membranes towards I_2 in I_2/KI solution, 5 mg of COF-$CuCl_2$ membranes were immersed into 10 mL of I_2/KI solution at different concentrations. The adsorption isotherms were obtained by plotting the values of q_e and q_e^{uc} versus the corresponding values of C_a^e and fitted by Langmuir and Freundlich models, respectively. The Langmuir model is based on the assumption that a monolayer

of adsorbate is uniformly adsorbed on the surface of the adsorbent, described in the Equation (7)

$$q_e = q_m K_L C_a^e / (1 + K_L C_a^e) \quad (7)$$

Where q_m (mg/g or g/mol) is the maximum adsorption capacity; K_L (L/mg) is Langmuir adsorption constant. The Freundlich model is based on the assumption of heterogeneous adsorption, described by Equation (8)

$$q_e = K_F (C_a^e)^{(1/n)} \quad (8)$$

where K_F is the Freundlich adsorption constant; 1/n is the adsorption strength.

1.2.3 Study of I_2 releasing process of I_3^-@COFs-$CuCl_2$ membranes in PBS solutions

After the adsorption of iodine in I_2/KI solution, the obtained I_2@COF-$CuCl_2$ membranes were removed and rinsed with H_2O for five times to remove the free I_2 from the membrane surface followed by drying in a fume hood. And then I_2@COF-$CuCl_2$ membranes were used for the following study of I_2 releasing process. The Uv-vis absorption spectrum was used to measure absorption value of different concentrations of iodine (0.005 mg/mL, 0.008 mg/mL, 0.01 mg/mL, 0.015 mg/mL, 0.02 mg/mL) in PBS solution. The UV-vis absorption peaks of I_2 in PBS solution were 203 nm and I_3^- in PBS solution were 288 nm and 350 nm. The characteristic absorption intensity of I_2 at 203 nm was simulated by a linear model to produce a standard curve of iodine in PBS solution, in which the equation y=49.2592x+0.02379 was obtained. (x is the concentration of I_2 in PBS solution; y is the UV-vis absorption value). According to this equation, we can calculate the I_2 concentration in PBS solution according to UV-vis absorption value. The I_2 concentration obtained at a given desorption time (C_d^t) was used to calculate the I_2 mass desorbed from the I_3^-@COF-$CuCl_2$ membranes with respect to the molar number of the COF-$CuCl_2$ unit cells (Q_t^{uc}, g/mol) according Equation (9)

$$Q_t^{uc} = (C_d^t \times V_d / M_{I2}) / W_{COF} \quad (9)$$

where V_d is the volume of PBS solution used for I_2 desorption from I_3^-@COFs-$CuCl_2$ membranes.

1.2.4 Study of the antibacterial activity of COF-$CuCl_2$ membranes

I_3^-@TpPa-$CuCl_2$ (18.4 mg), I_3^-@TpBD-$CuCl_2$ (18.8 mg), and I_3^-@TpTD-$CuCl_2$ (19.6 mg) membranes adsorbed with 2 mg of I_2 were placed into the culture tubes containing 10 mL of 2×10^8 CFU/mL of *E. coli or* 10 mL of 3×10^8 CFU/mL of *S. aureus*, and then the bacterial solution were placed in a constant temperature oven at 37 °C for a period of time. After incubation, 100 μL of bacterial solution was taken out and spread on agar plates, followed by 24 h incubation in 37 ℃ for bacterial colonization. The number of *E. coli* colonies formed on the agar plates were used to assess the antibacterial performance of the I_3^-@COF-$CuCl_2$ membranes.

For the Zone of inhibition (ZOI) test of the antibacterial performance of I_3^-@COF-$CuCl_2$ membranes, I_3^-@TpPa-$CuCl_2$ (9.2 mg), I_3^-@TpBd-$CuCl_2$ (9.4 mg), and I_3^-@TpTd-$CuCl_2$ (9.8 mg) membranes with 1 mg of adsorbed iodine and TpTd-$CuCl_2$ membrane without iodine loading were placed on agar plates coated with 0.3 mL of 108 CFU/mL of *S. aureus*, respectively. Then the agar plate was incubated in a constant temperature oven at 37 ℃ for 12 h. And then the agar plates were taken out and the ZOIs atop was measured to test the ability of the I_3^-@COF-$CuCl_2$ membranes to inhibit the growth of *S. aureus*.

1.3 Characterization

UV-vis absorption spectroscopy was performed on a UV-2450 spectrophotometer (HITACHI, Japan). Nitrogen adsorption-desorption isotherms of COF-$CuCl_2$ membranes were measured by Quantachrome Autosorb-iQ2 analyzer (Quantachrome Instruments U.S.). The C, N and H contents of COF-$CuCl_2$ membranes were determined by using a CHNOS analyzer (Vario EL cube, Elementar, Germany). The Cu content of the COF-$CuCl_2$ membranes was measured by means of inductively coupled plasma atomic emission spectrometer (ICP-OES, iCAP 7600, Thermo Fisher Scientific, U.S.). In this case, 10 mg of as-prepared COF-$CuCl_2$ were decomposed in 8 mL of aqua regia at 120 °C overnight in a hydrothermal autoclave reactor, which was diluted to 100 mL of aqueous solution with water prior to ICP analysis. The XRD patterns of the COFs and COF-$CuCl_2$ membranes were obtained on a X-ray diffractometer under 40 kV, 200 mA with a scanning rate of 1° min^{-1} (2θ) (Empyrean PANalytical B.V. Japan). Their surface morphology were characterized by means of field emission scanning electron microscope (FE-SEM, SU4800, Hitachi, Japan). XPS spectroscopy was carried out on a Thermo Scientific K-Alpha XPS (XPS, ESCALAB 250, Thermofisher U.S.) with a characteristic energy of 1486.7 Ev. Thermogravimetric analysis (TGA) was performed on Netzch Sta 449c thermal analyzer system in the temperature range from 30 °C to 800 °C at a heating rate of 10 °C min^{-1} in air. Raman spectroscopy was carried out on a Horiba LabRAM HR evolution instrument in the wavenumber range of 50-4000 cm^{-1} by using 785 nm laser (50 mW).

2. Supplementary Figures

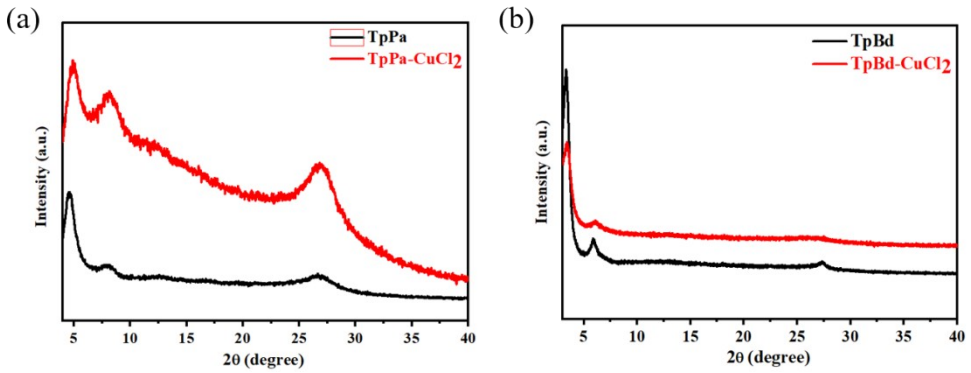

Figure S1 (a) XRD patterns of TpPa-$CuCl_2$ (red) and TpPa (black) membranes. (b) XRD patterns of TpBd-$CuCl_2$ (red) and TpBd (black) membranes.

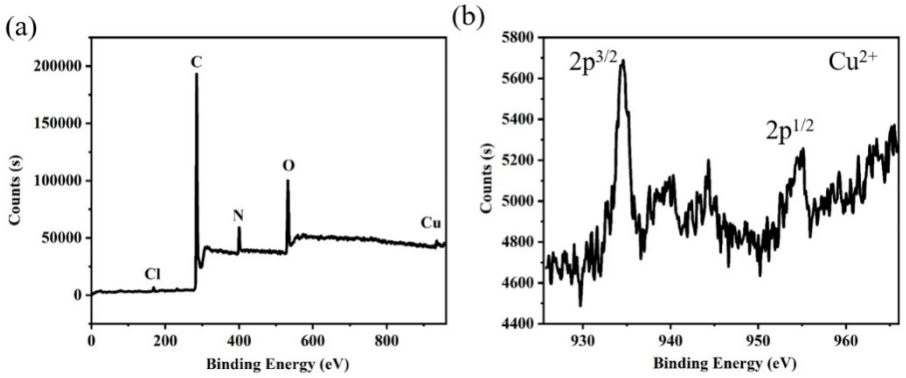

Figure S2 (a) XPS of TpTd-$CuCl_2$ membranes. (b) The high-resolution spectra for Cu $2p^{3/2}$ and $2p^{1/2}$ corresponding to Cu^{2+}.

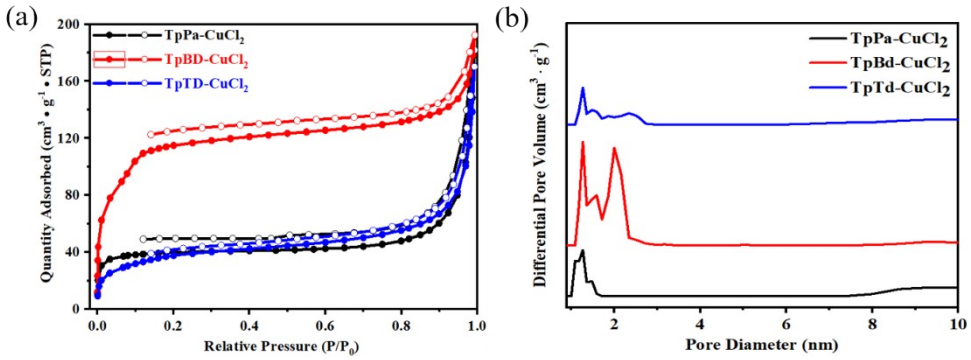

Figure S3 (a) Nitrogen adsorption-desorption isotherms curves of TpPa-$CuCl_2$, TpBd-$CuCl_2$, and TpTd-$CuCl_2$ membranes (filled circles: adsorption, open circles: desorption) (b) The pore size distribution of TpPa-$CuCl_2$, TpBd-$CuCl_2$, and TpTd-$CuCl_2$ membranes.

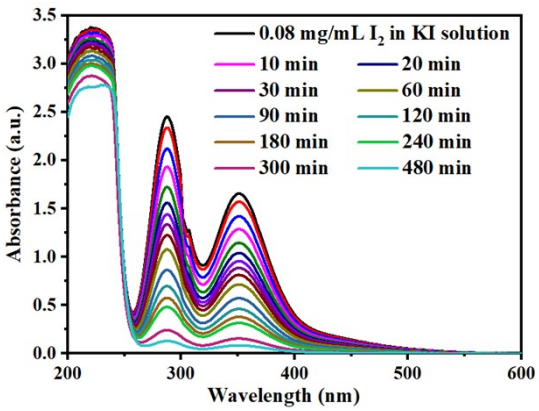

Figure S4 Temporal absorption spectral evolution of 10 mL aqueous solution of I_2/KI at the initial concentration of 0.08 mg/mL of I_2 recorded after 5 mg of TpTd-$CuCl_2$ membrane are placed inside.

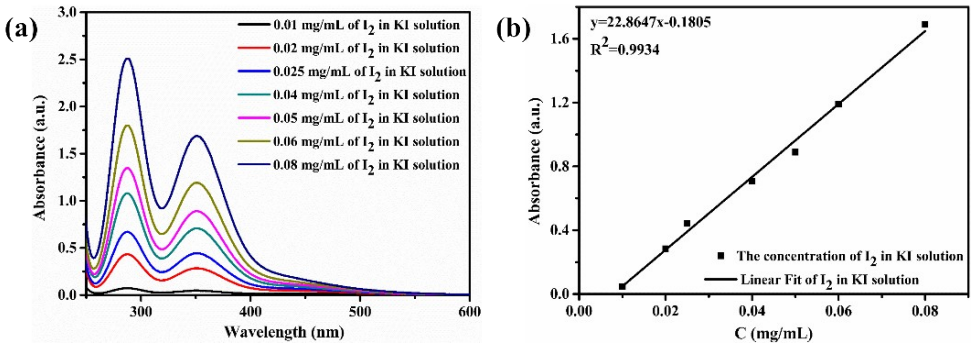

Figure S5 (a) UV-vis spectra of I_2/KI solutions containing different concentration of I_2 (b) Plot of the absorbance intensity of I_2/KI aqueous solution at 350 nm versus I_2 concentration, which can be well fitted by a linear function.

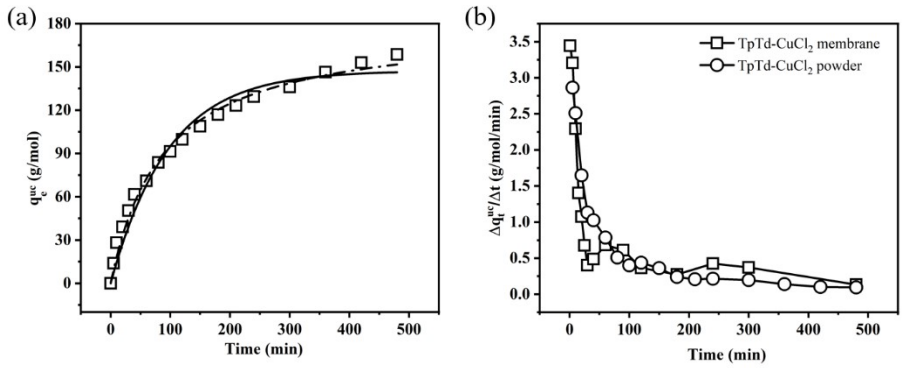

Figure S6 (a) The values of q_t^{uc} are plotted against time for the adsorption kinetics of TpTd-$CuCl_2$ powder, which were fitted using pseudo-first-order (solid curves) and pseudo-second-order (dash curves) kinetic models. (b) Iodine adsorption rate ($\Delta q_t^{uc}/\Delta t$) of TpTd-$CuCl_2$ membrane (square), TpTd-$CuCl_2$ powder (circle) in KI/I_2 aqueous solution.

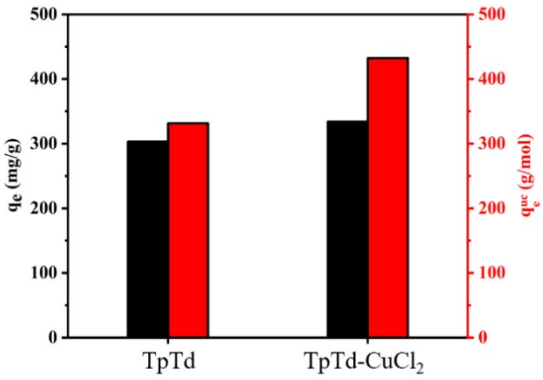

Figure S7 The values of adsorption capacity with respect to mass (q_e, black) and molar number of unit cell (q_e^{uc}, red) of TpTd-$CuCl_2$ membrane, in which the initial concentration of I_2 in KI/I_2 aqueous solution is 0.25 mg/mL.

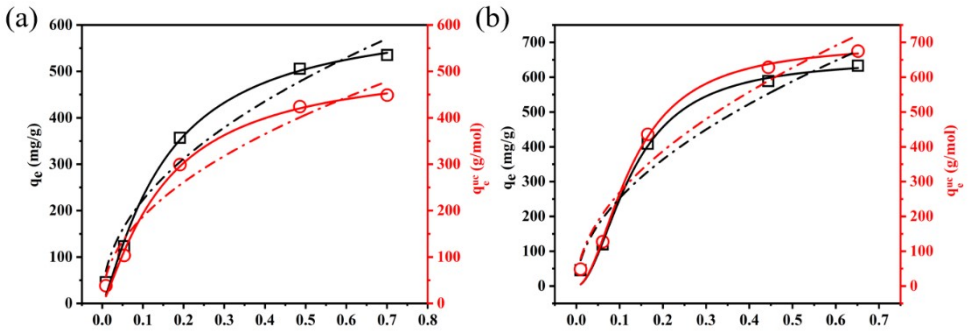

Figure S8 Adsorption isotherms of TpPa-$CuCl_2$ (a) and TpBd-$CuCl_2$ (b) membranes in KI/I_2 aqueous solution obtained by the values of q_e (black square) and q_e^{uc} (red circle) at different equilibrium I_2 concentration, which are fitted by Langmuir (solid curves) and Freundlich models (dashed curves).

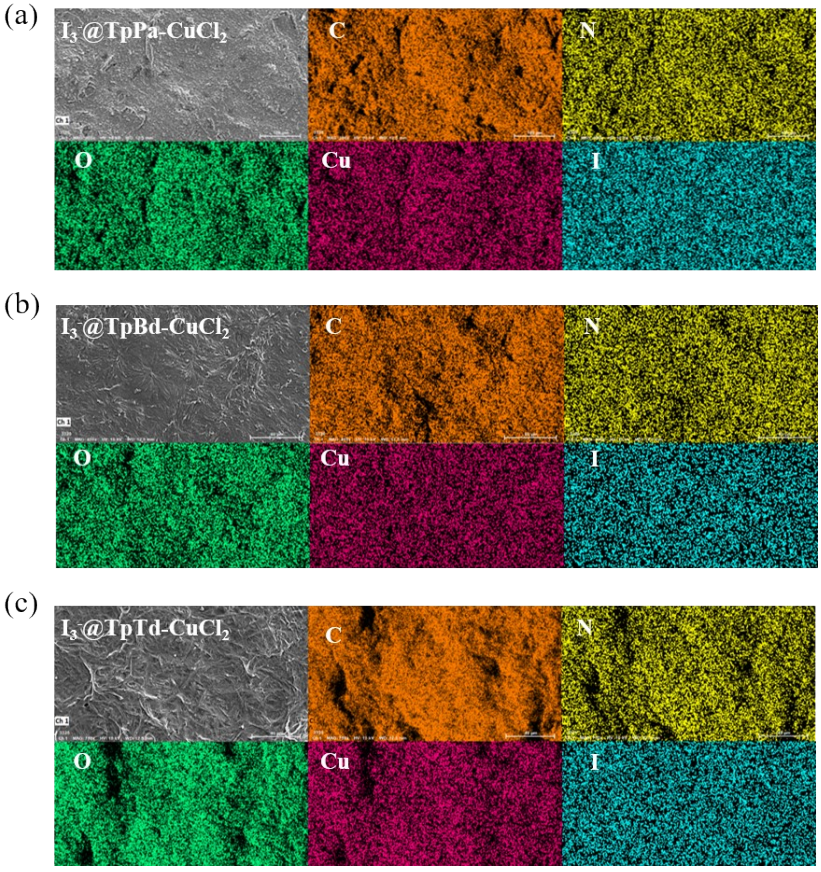

Figure S9 SEM and EDS element (C, N, O, Cu, I) mapping images of the I_3^-@TpPa-$CuCl_2$, I_3^-@TpBd-$CuCl_2$ and I_3^-@TpTd-$CuCl_2$ membranes, which demonstrate the uniform distribution of iodine across the membranes.

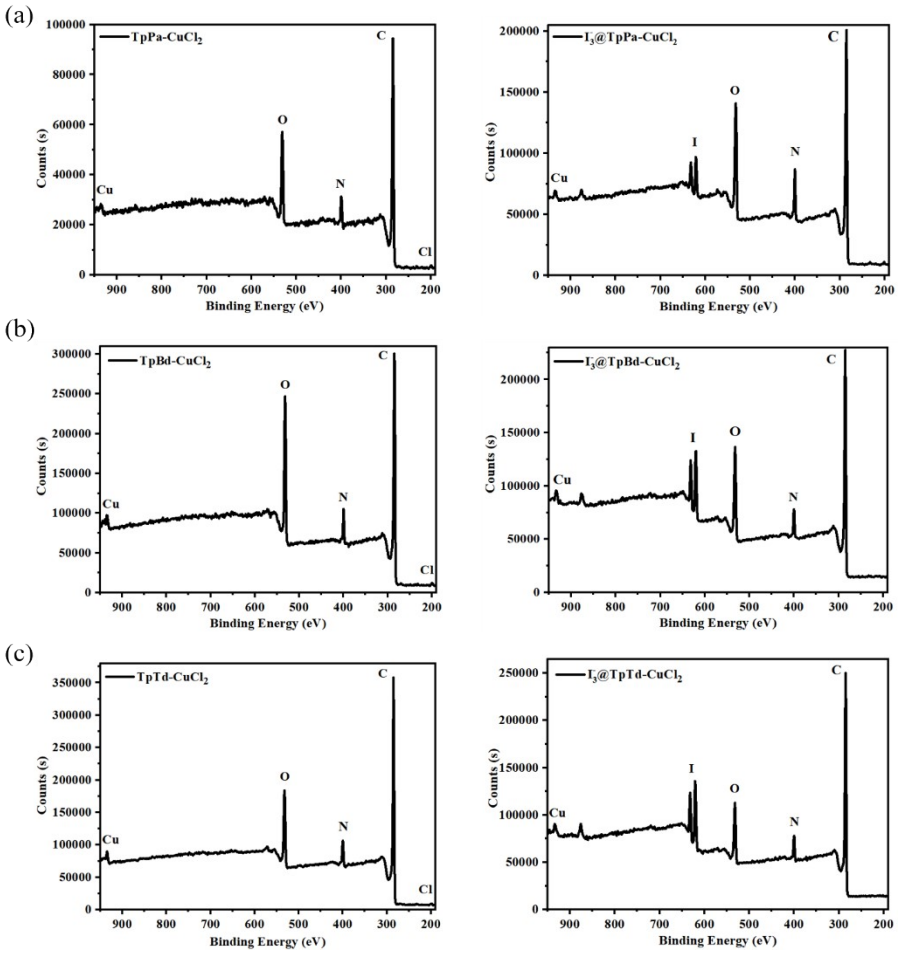

Figure S10 XPS spectra of TpPa-$CuCl_2$ and I_3^-@TpPa-$CuCl_2$ (a), TpBd-$CuCl_2$ and I_3^-@TpBd-$CuCl_2$ (b), TpTd-$CuCl_2$ and I_3^-@TpTd-$CuCl_2$ (c) membranes, in which the peaks of C, N, O, Cu, Cl and I are marked.

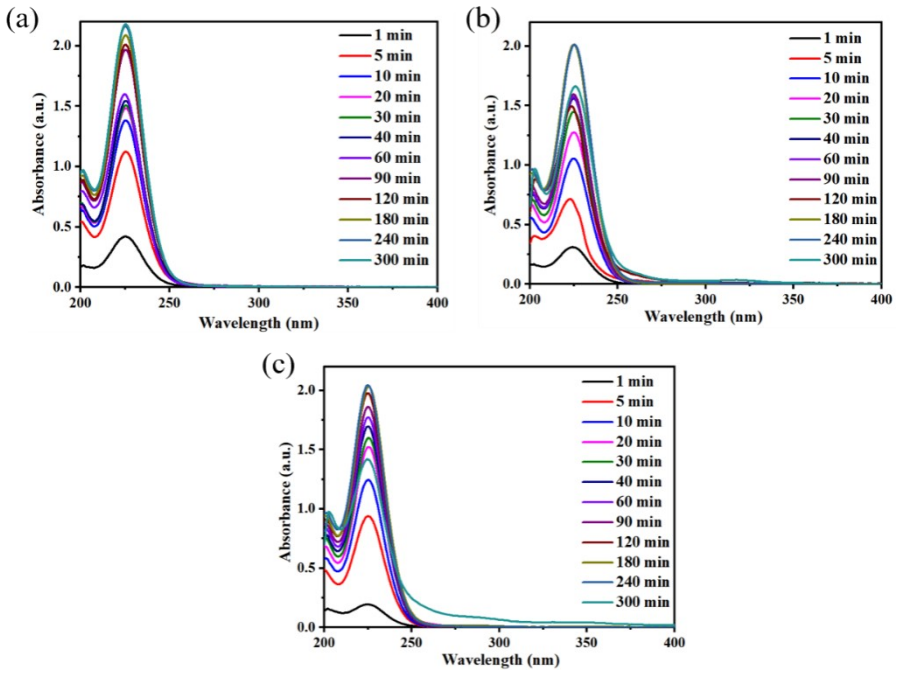

Figure S11 Temporal evolution of the absorption spectra of PBS solution during incubation of I_3^-@TpPa-Cu (a), I_3^-@TpBd-Cu (b) and I_3^-@TpTd-Cu (c) membranes to record the I_2 release process.

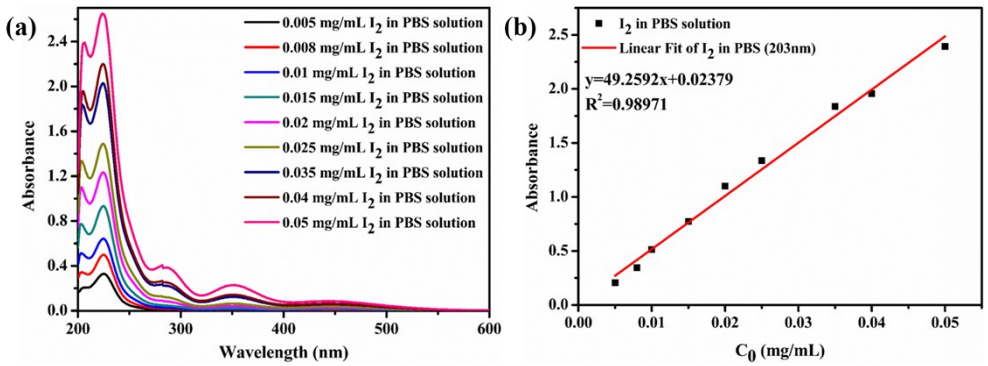

Figure S12 (a) UV-vis absorption spectra of PBS solution of I_2 at concentration (C_0) ranging from 0.005 to 0.05 mg/mL. (b) Plot of the I_2 absorbance intensity at 203 nm (I_{203}) in Figure a versus I_2 concentration, which can be well fitted by a linear function.

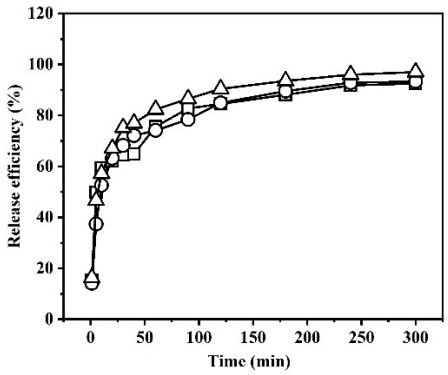

Figure S13 Iodine release efficiency of I_3^-@TpPa-Cu (square), I_3^-@TpBd-Cu (circle), and I_3^-@TpTd-Cu (triangle) membranes versus time in PBS solution.

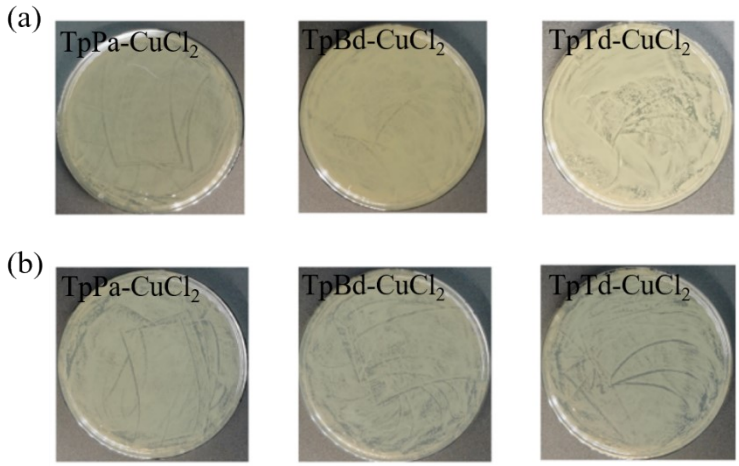

Figure S14 (a) Optical photographs of *E. coli.* colonies on agar plates obtained after 24 h incubation of 100 μL of bacterial solutions taken out from 10 mL of 10^8 CFU/mL of *E. coli.*, where COF-$CuCl_2$ membranes are placed for 12 h. (b) Optical photographs of *S. aureus* colonies on agar plates obtained after 24 h incubation of 100 μL of bacterial solution taken out from 10 mL of 10^8 CFU/mL of *S. aureus*, where COF-$CuCl_2$ membranes are placed for 12 h.

3. Supplementary Tables

Table S1 Summary of the C, H, N, Cu content (weight, %) and the molar ratio of N to Cu of TpTd-$CuCl_2$.

	C	**H**	**N**	**Cu**	Molar ratio of N to Cu
TpTd-$CuCl_2$	79.51 %	4.98 %	6.91 %	8.61 %	3.67:1

Table S2 Summary of the q_e value of TpTd-$CuCl_2$ membranes obtained by 8 h adsorption at initial concentration of 0.08 mg/mL and those calculated by fitting of their adsorption kinetics profiles according to pseudo-first-order or pseudo-second-order models.

COF-$CuCl_2$ membrane	exp. q_e/mg·g^{-1}	Pseudo-first-order model			Pseudo-second-order model		
		cal. q_e /mg·g^{-1}	k_1 /min^{-1}	r^2	cal. q_e /mg·g^{-1}	k_2 /min^{-1}	r^2
TpTd-$CuCl_2$	137.42	120.28	0.025	0.958	138.87	2.082E-4	0.989

Table S3 Summary of the q_e^{uc} value of TpTd-$CuCl_2$ membranes obtained by 8 h adsorption at initial concentration of 0.08 mg/mL and those calculated by fitting of their adsorption kinetics profiles according to pseudo-first-order or pseudo-second-order models.

COF-$CuCl_2$ membrane	exp. q_e^{uc}/g·mol^{-1}	Pseudo-first-order model			Pseudo-second-order model		
		cal. q_e^{uc} /g·mol^{-1}	k_1 /min^{-1}	r^2	cal. q_e^{uc} /g·mol^{-1}	k_2 /min^{-1}	r^2
TpTd-$CuCl_2$	173.46	155.72	0.025	0.958	179.78	1.608E-4	0.989

Table S4 Summary of the fitting results of I_2 adsorption isotherms in terms of q_e (mg/g) of COF-$CuCl_2$ membranes in KI/I_2 solution obtained according to Langmuir and Freundlich models.

COF	Langmuir model			Freundlich model		
	q_{max} /mg·g^{-1}	K_L /mL·mg^{-1}	r^2	K_F /mg$^{1-1/n}$g^{-1}mL$^{1/n}$	1/n /g·L^{-1}	r^2
TpPa-$CuCl_2$	625.0	9.83	0.990	677.6	0.483	0.952
TpBd-$CuCl_2$	655.2	48.8	0.987	846.8	0.526	0.925

TpTd-$CuCl_2$	746.8	36.8	0.987	936.4	0.424	0.900

Table S5 Summary of the fitting results of I_2 adsorption isotherms in terms of q_e^{uc} (g/mol) of COF-$CuCl_2$ membranes in KI/I_2 solution obtained according to Langmuir and Freundlich models.

COF	Langmuir model			Freundlich model		
	q_{max}^{uc} /g· mol^{-1}	K_L /mL·mg^{-1}	r^2	K_F /$mg^{1-1/n}g^{-1}mL^{1/n}$	1/n /g·L^{-1}	r^2
TpPa-$CuCl_2$	523.9	9.84	0.990	568.1	0.483	0.952
TpBd-$CuCl_2$	698.7	48.8	0.987	903.0	0.526	0.925
TpTd-$CuCl_2$	966.8	36.8	0.987	1212.3	0.424	0.900

Table S6 Comparison of the antibacterial performance of I_3^-@TpPa-Cu, I_3^-@TpBd-Cu and I_3^-@TpTd-Cu membrane with other work reported in the literature by means of zone of inhibition (ZOI) test.

Materials	Zone of inhibition (*S. aureus*) (cm)	Reference
I_3^-@TpPa-Cu	**0.3**	**This work**
Neat PVA membrane	0.5	S3
I_3^-@TpBd-Cu	0.6	**This work**
PVA-*C. longa*	0.7	S4
I_3^-@TpTd-Cu	**0.8**	**This work**
BC-Ag	0.95	S5
PVA/Cu (Nanofiber reduction)	1.0	S3
PVA/Cu (Solution reduction)	1.2	S3
BC-Ag-MMT	1.24	S5
AY2	1.4	S6
PVA/Cu (Immersion method)	1.5	S3
SOJ-coated gauze pads	1.6	S7
SOJ-coated N6 nanofibers	1.65	S7
AY3	1.8	S6

CCN-COS-AgNP/PVA	2.3	S8
AY4	2.5	S6
PVA-*A. indica*	2.6	S4

4. Reference

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