

Supporting Information

Construction Self-propelled Micromotor for “hunting bacteria”

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1. Experimental Section/Methods

1.1. Materials

2-isocyanatoethyl methacrylate (IEMA, AR), dibutyltin dilaurate (DBTDL, AR), 3-methacrylamido-N,N,N-trimethylpropan-1-aminium chloride (AR, 50% in water) and 5-Hydroxymethylthiazole (5-HMT, AR) were purchased by Shanghai Macklin Biochemical Co., Ltd. Cobalt nitrate ($\text{Co}(\text{NO}_3)_2$, AR) and silver nitrate (AgNO_3) were purchased by Baiyin Chemical Reagent Factory. Sodium alginate (SA, AR) and Agar were purchased from Tianjin Guangfu Fine Chemical Research Institute. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR, Xilong Chemical Co., Ltd), 2-Methylimidazole (2-MIm, AR, Aladdin), tetracycline (TC, AR, Shanghai Yuanye Biotechnology Co., Ltd) and nutritional agar (Qingdao High-tech Industrial Park Haibo Biological Co., Ltd) were obtained commercially. *Escherichia coli* (E. coli) and *Staphylococcus aureus* (S. aureus) were accepted from Microbiology Laboratory, School of Life Sciences in our university.

1.2. Characterization

The composition and structure of products and comparisons were analyzed by FT-IR, and pure KBr was used as the reference sample. The phase constituents of the nanostructures were analyzed by X-ray diffraction (XRD, Dmax-2400, Cu K radiation, Japan Science & Technology Co., Ltd.). Scanning electron microscope (SEM, 5 kV, ULTRA Plus microscope, Germany) was used to analyze surface morphologies. Transmission electron microscopies (TEM, JEOL JEM1230 microscope, Japan) equipped with energy-dispersive spectroscopy (EDS) was used to observe the morphology and size of the SPM. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI) was used to determine the surface composition. Specific surface area, pore capacity, and pore diameter were tested by the micrometrics surface area analyzer (BET, ASAP2020, Barret-Joyner-Halenda (BJH) equation, 77 K). The surface hydrophilicity was analyzed on a contact angle instrument (SL200B, China). Self-propelled performance of SPM was tested by optical microscopy (DM5000/DFC450/LAS).

1.2. Synthesis of BiOFs and its comparisons.

1.2.1. Synthesis of BiOFs

The procedure for synthesis of microimpeller-shaped bimetallic organic frameworks (BiOFs) containing Co (II) and Zn (II) is as following: First, $\text{Co}(\text{NO}_3)_2$ (0.346 g) and 2-MIm (1.301 g) was dissolved in distilled water (40 mL) under stirring. Then, 0.05 g of SA added with high-speed stirring, and further stirred for 30 min. Second, 40 mL of zinc aqueous solution containing 0.147 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was pour into above solution under vigorous stirring conditions. After reacting for 6 h with gently stirring, the product was obtained. The crude products were separated by centrifugation, and further washed by absolute ethanol and distilled water for 6 times, respectively. Finally, the powders of pure BiOFs were obtained after freeze-drying.

1.2.2. Synthesis of SA-ZIF(Co)

The MOFs with single metal (Co II) (SA-ZIF(Co)) was synthesized with similar procedure of BiOFs: Typically, in 40 mL aqueous solution containing $\text{Co}(\text{NO}_3)_2$ (0.346 g) and 2-MIm (1.301 g), 0.05 g of SA was added with quickly stirring, and further stirred for 30 min. Then, the mixture was stirred for 6 hrs. SA-ZIF(Co) was obtained as the same way of BiOFs.

1.2.3. Synthesis of SA-ZIF(Zn)

The MOFs with Zn (II) (SA-ZIF(Zn)) was synthesized with same procedure of SA-ZIF(Co), which 0.147 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used for replacing $\text{Co}(\text{NO}_3)_2$. The white powder of SA-ZIF(Zn) was obtained.

1.2.4. Synthesis of ZIF(Co, Zn)

The MOFs containing Co (II) and Zn (II) without natural polymer inducer (ZIF(Co, Zn)) was synthesized with same procedure of BiOFs, which SA was not added. The product was recorded as ZIF(Co, Zn).

1.3. Synthesis of SPM, PoTZ and their comparisons

1.3.1. Synthesis of acrylic thiazole (AcTZ)

AcTZ was synthesized as reported method ^[S1] by using 5-HMT (4.6 g, 0.04 mol), and IEMA (6.2 g, 0.04 mol) as materials, acetone as solvents and DBTDL as catalysts. The yield of AcTZ was 7.3 g, and its data of FTIR spectra: $\tilde{\nu}(\text{cm}^{-1})$ 3291, 1745, 1630, 1175, 1123, 1072, 810, 758.

1.3.2. Synthesis of SPM and PoTZ

The procedure for synthesis of self-propelled micromotor (SPM) is as following: First, in a three-necked flask (100 mL) containing 30 mL of alcohol-water solution (EtOH/H₂O: 1/1), 0.88 g of AcTZ and 0.20 g of BiOFs was added with stirring and nitrogen protection. The mixture was further stirred for 3 h under nitrogen gas. Second, the fresh AIBN/EtOH solution (5 mL) containing 0.044 g AIBN was drop-wise added into above mixture. Then, the system was moved into heating bath at 60 °C and reacting 12 h with slightly stirring for in-situ polymerization and assembly. The crude products were separated by centrifugalizing, and washed with water and ethanol, respectively. SPM was obtained after freeze-drying. PoTZ was obtained without addition of BiOFs.

1.3.3. Synthesis of PQAs and PQAs-BiOFs

Following the same method, using 3-methacrylamido-N,N,N-trimethylpropan-1-aminium chloride as typical active monomer of quaternary ammonium salt (QAs), and KPS as initiator, PQAs and PQAs-BiOFs were obtained.

1.3.4. Synthesis of P(QAs-TZ) and P(QAs-TZ)-BiOFs

Meanwhile, under the initiator of AIBN (0.082 g), the copolymerization between AcTZ (EtOH, 20 mL) and QAs was developed in-situ on surface and pores of BiOFs, P(QAs-TZ) and P(QAs-TZ)-BiOFs were prepared.

1.4. Antibacterial performance

The antibacterial performance was tested using the method of plate colony counting as previously reported procedure.^[S2] Typically, the same volume of 5 mg/mL SPM and the bacterial suspension (1×10⁷ CFU/mL) were added on an ultra-clean nutrient agar plate. Then, the mixture solution was spread on nutrient agar plates uniformly, and the plates were incubated at 37 °C for 24 h. The bactericidal efficacy of samples was evaluated. The control group was the corresponding bacterial suspension without samples treatment.

1.5. Minimum Inhibitory Concentration (MIC)

The antimicrobial potency of functional materials was quantitatively evaluated by the optical density (OD) method. Samples were added to 5 mL bacterial cultures (1×10⁷ CFU mL⁻¹) at different concentrations (0, 0.2, 1.6, 3.2, 6.4, 12.0, and 15.0 mg/mL). Then, these bacterial mixtures solution were shaken at 37 °C for 24 h. The absorbance value of samples at each concentration was measured at 600 nm as reference.

1.6. Self-propelled antibacterial performance test

The bacterial suspension (1×10^7 CFU/mL) contact with SPM at the speed of V1 and V2, respectively. A certain amount of the outflow of mixed liquid was added on an ultra-clean nutrient agar plate. Then, the mixture solution was spread on nutrient agar plates uniformly, and the plates were incubated at 37 °C for 12 h. And the control group contained no SPM.

1.7. Antibacterial cycle stability test

The durability of nanomaterial antibacterial activity was evaluated by Colony-forming unit counting. 3.0 mL samples (6.4 mg/L) were dropped into 3.0 mL of bacteria suspension (10^6 CFU/mL). They were then incubated in a shaker at 37 °C for 5 days. In addition, the bacteria suspension was centrifuged and replaced with the new at every day. Subsequently, the treated bacteria suspension was transferred to a solid medium for incubation at 37 °C for 12 h. Finally, the numbers of colonies were photographed and counted, and each assay was carried out in triplicate. The final product was characterized by FTIR, XRD and SEM.

1.8. Bacterial Morphology

The morphology of bacteria was observed by SEM. The bacterial suspension of *E. coli* (1×10^7 CFU mL⁻¹) was cultured at 37 °C at a constant temperature shock for at least 24 h. Then, it was centrifuged in a refrigerated centrifuge at 8 °C at 4000 rpm for 5 min. After removing the supernatant, the deposits were washed by an appropriate amount of PBS solution (pH 7.2-7.4) for 3 times. Then, the bacteria were fixed with 2.5% glutaraldehyde solution for 3 h, and washed with PBS solution for 3 times. The obtained products were dehydrated for 15 min with 25%, 75%, 90%, and absolute ethanol each. Finally, the treated samples were detected by SEM.

1.9 Application of antimicrobial agents to coatings and coatings

The antibacterial application of SPM was tested by using the method of plate colony counting. The MIC of SPM was mixed with coating and dyes, respectively. The bacterial suspension (1×10^7 CFU/mL) and above mixture were added on an ultra-clean nutrient agar plate. Then, the mixture solution was spread on nutrient agar plates uniformly, and the plates were incubated at 37 °C for 24 h. The bactericidal efficacy of samples was evaluated. The control group was the corresponding bacterial suspension

and coating and dyes, which was not treated with SPM.

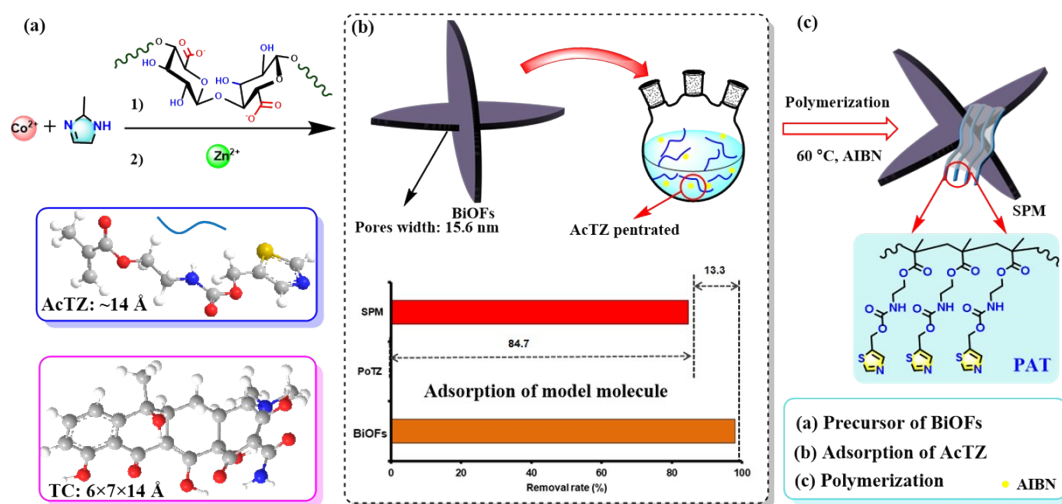


Fig. S1 The position of PoTZ in SPM

Tab. S1 The main formulation for synthesis of SPM and other products

No.	2-MIm (mmol)	Co ²⁺ (mmol)	Zn ²⁺ (mmol)	SA (g)	H ₂ O (mL)	Products
1	16.0	1.9	0.5	0.05	80	BiOFs
2	16.0	1.9	0.5	/	80	ZIF(Co, Zn)
3	16.0	1.9	/	/	40	SA-ZIF(Co)
4	16.0	/	0.5	0.5	40	SA-ZIF(Zn)

Tab. S2 The main formulation for synthesis of polymer and its conjugate products

No.	BiOFs (g)	QAs (g)	AcTZ (g)	Initiator (g)	EtOH/H ₂ O (mL)	products
1	0.2	/	0.88	AIBN (0.044)	40	SPM
2	/	/	0.88	AIBN (0.044)	40	PoTZ
3	0.2	1.5	0	KPS (0.038)	40	PQAs-BiOFs
4	0.2	1.5	0.88	AIBN (0.082)	60	P(QAs-TZ)-BiOFs
5	/	1.5	0.88	AIBN (0.082)	60	P(QAs-TZ)
6	/	1.5	0	KPS (0.038)	40	PQAs

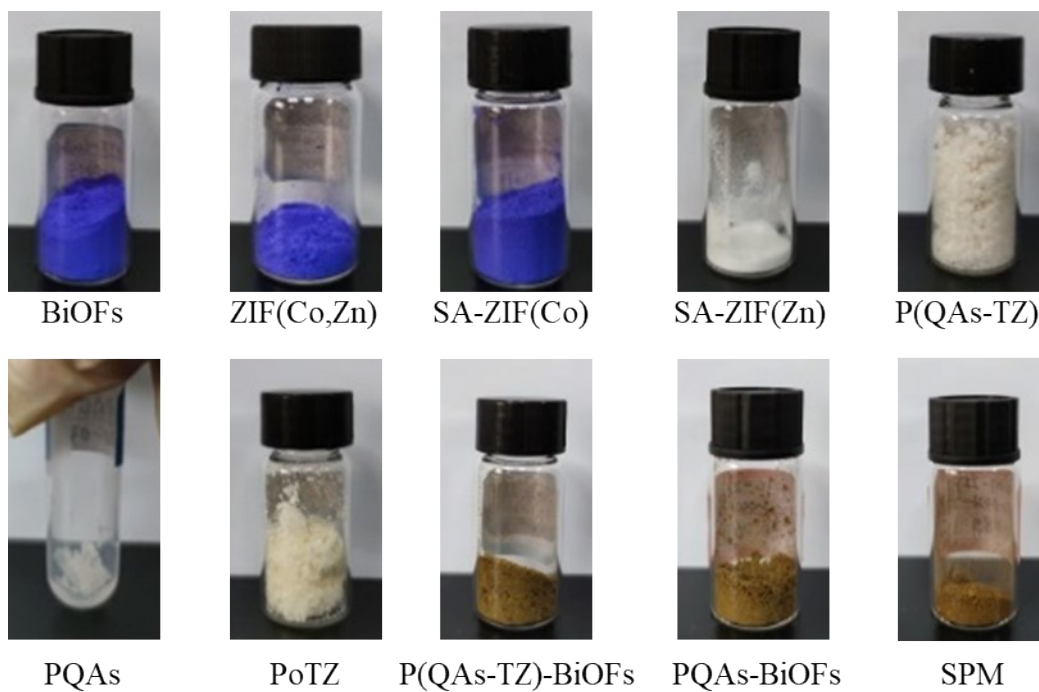


Fig. S2 Appearance (digital photos) of main products and comparisons

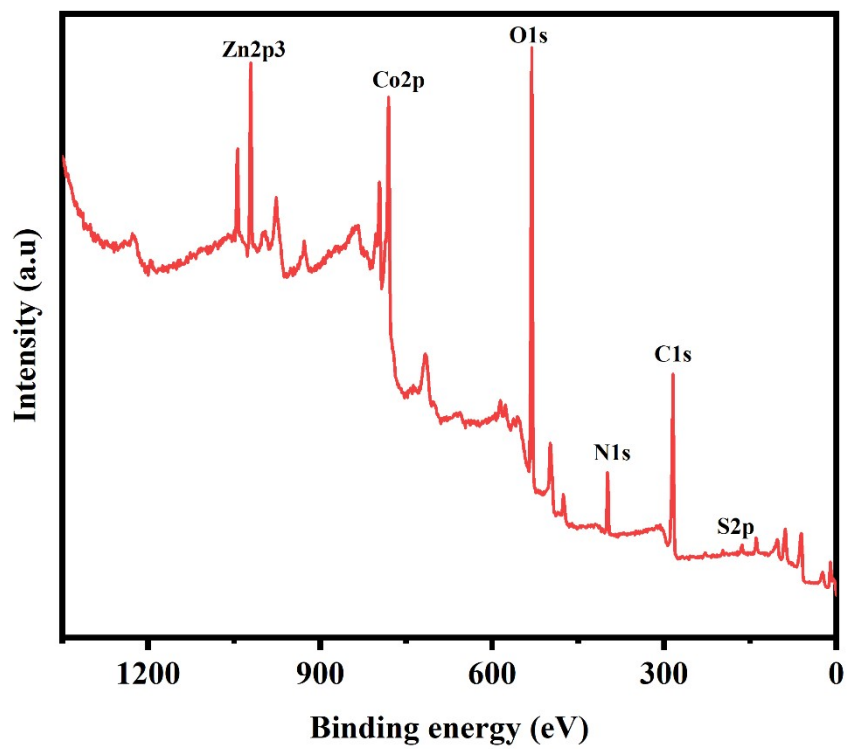


Fig. S3 XPS full spectrum of SPM

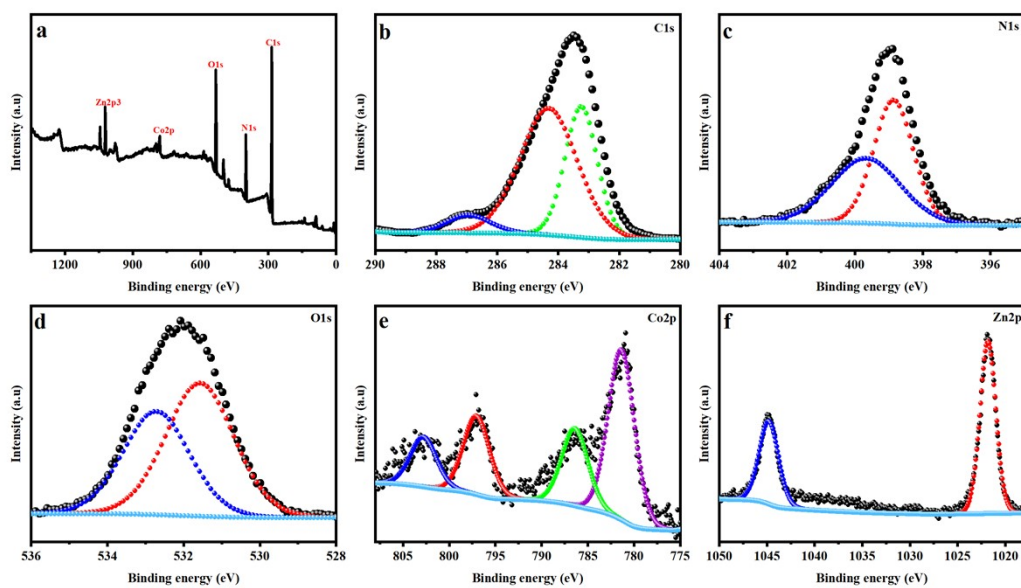


Fig. S4 XPS full spectrum of BiOFs (a) and its fine spectra of C1s (b), N1s (c), O1s (d), Co2p (e), Zn2p (f).

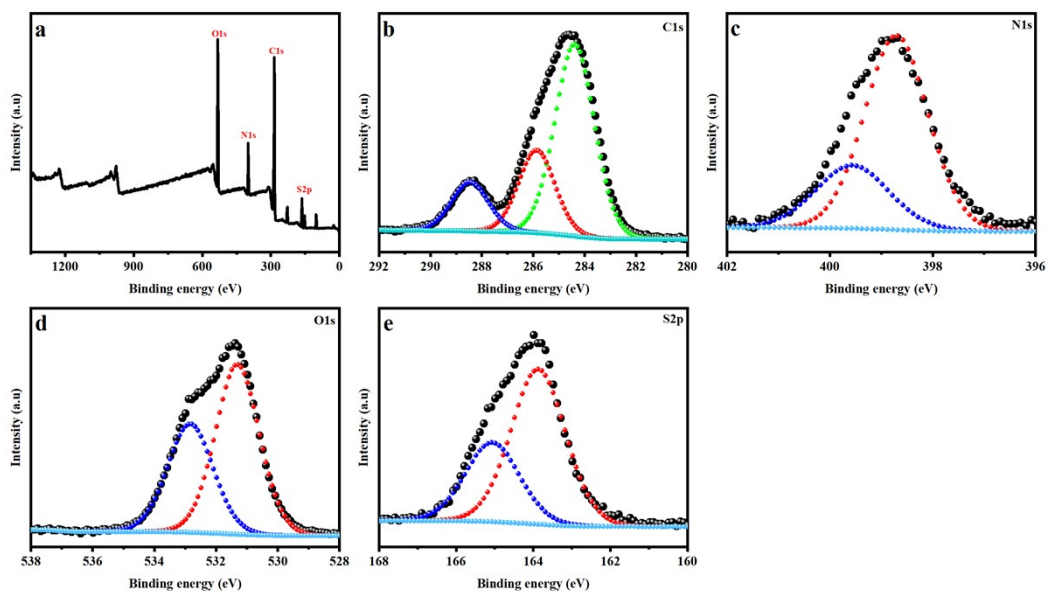


Fig. S5 XPS full spectrum of PoTZ (a) and its fine spectra of C1s (b), N1s (c), O1s (d), S2p (e)

Fourier-transform infrared spectroscopy (FT-IR) spectra of SPM were measured and compared with its intermediates (BiOFs, PoTZ) (Fig. S6a). In SPM, the asymmetrical telescopic vibration peak of COO⁻ on the SA chain appeared at 1405 cm⁻¹. The characteristic peaks at 3291 cm⁻¹ and 745 cm⁻¹ were mainly attributed to telescopic vibration of N-H and the non-planar rocking vibration absorption peak of N-H, respectively. The peaks at 758 and 810 cm⁻¹ were mainly attributed to the vibration of C-S in the heterocyclic thiazole ring. [S3] The characteristic peaks at 1072 and 1175 cm⁻¹ were accounted by the telescopic vibrations of C-N unique to thiazole and imidazole [S1], and the characteristic peak at 1630 cm⁻¹ could be corresponded to the vibration of C=N [S4]. The peak at 1123 cm⁻¹ was caused by the vibration of C-O-C. Meanwhile, the vibration peak of C=O at 1745 cm⁻¹ was also observed, mainly because of the formation of ester bonds present on the thiazole chain.

The synthesized self-propelled micromotor were identified via X-ray diffraction (XRD) and also compared with its intermediates (Fig. S6b). For SPM, the characteristic peaks at 10.9°, 17.9° and 28.9° indicated the existence of BiOFs. The re-assembly during the polymerization reaction at 60 °C caused the lower intensity in micromotor. It was also observed that PoTZ exhibited high crystallinity, and strong diffraction peaks appeared at 6.7°, 13.3°, 18.7°, 21.7°, 22.6°, and 26.0°. After being in-situ polymerized along with interaction with BiOFs, its characteristic peaks were also weakened because the polymer chains of PoTZ penetrated into the pores and surface of BiOFs. Certainly, comparison with pure Co-ZIF and Zn-MOF (CCDC 671074 and JDDS#00-062-1030) at 2θ=7.4°, 12.7°, and 18.2° [S5] could not be found that neither in BiOFs nor SPM, which demonstrated that the existence of SA and Zn²⁺ constructed an unparalleled BiOFs, and the SPM was also prepared by conjugating BiOFs with polymer.

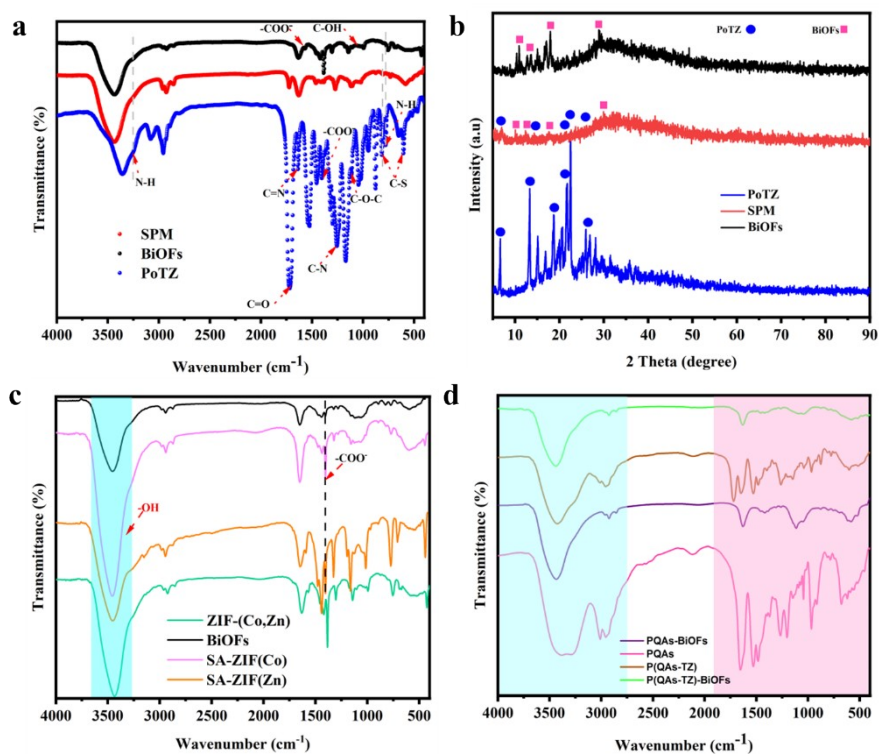


Fig. S6 FT-IR and XRD of products. FT-IR (a) and XRD (b) of BiOFs, PoTZ and SPM (IR (SPM): $\tilde{\nu}$ =745 (m), 758 (m), 810 (m), 1072 (s), 1123 (w), 1175 (m), 1630 (m), 1745 (vs) 3291 (br) cm^{-1}); And the FT-IR of BiOFs, SA-ZIF(Co), SA-ZIF(Zn) and ZIF(Co, Zn) (c) and PQAs, PQAs-BiOFs, P(QAs-TZ) and P(QAs-TZ)-BiOFs (d).

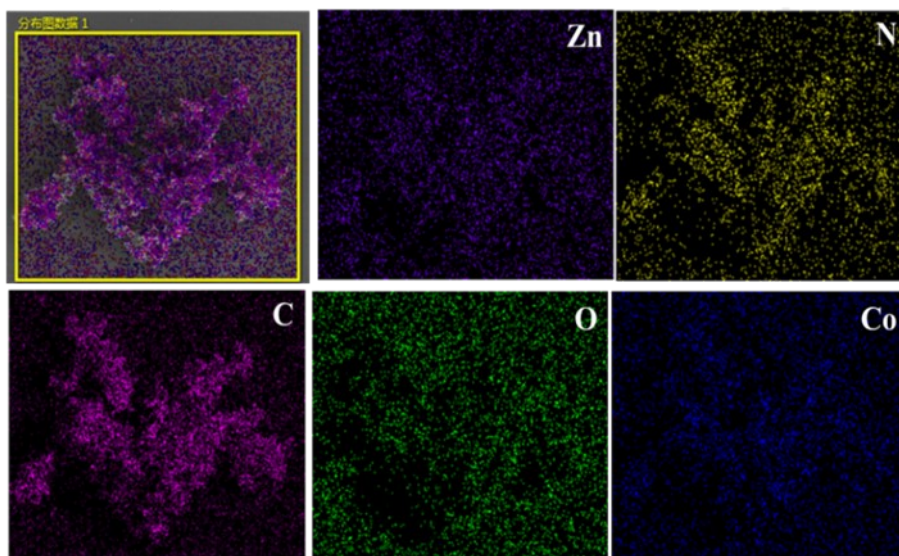


Fig. S7 The EDS of BiOFs

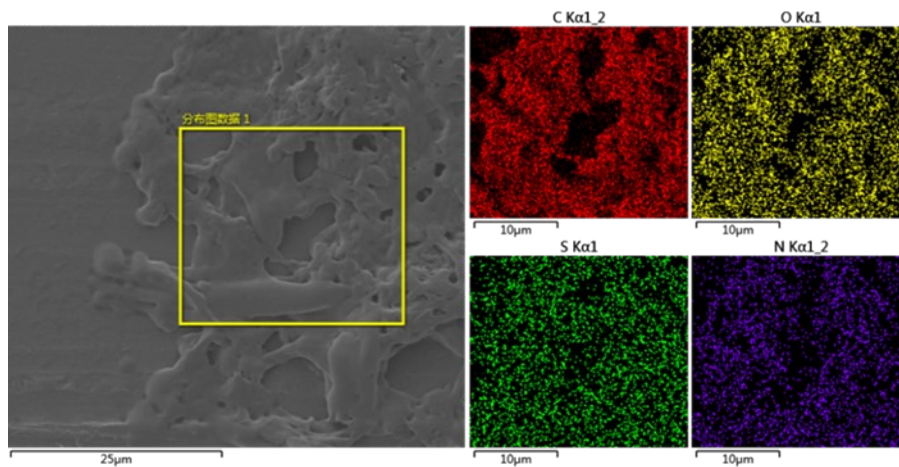


Fig. S8 The EDS of PoTZ

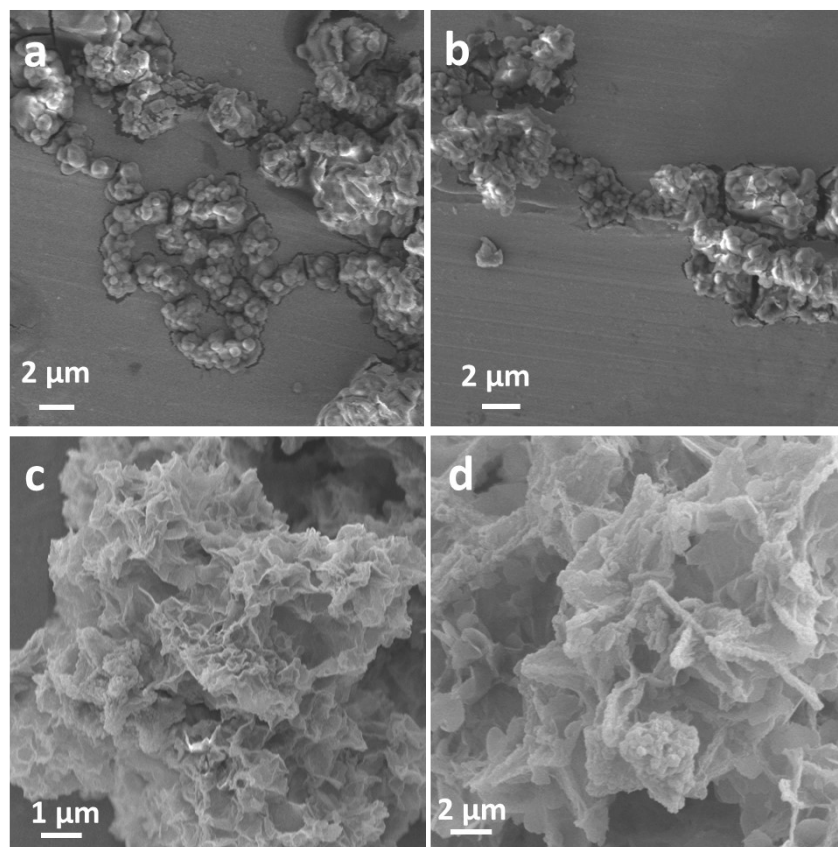


Fig. S9 SEM images of other samples. SEM images of PQAs (a), P(QAs-TZ) (b), and their BiOFs composites: PQAs-BiOFs (c), P(QAs-TZ)-BiOFs (d)

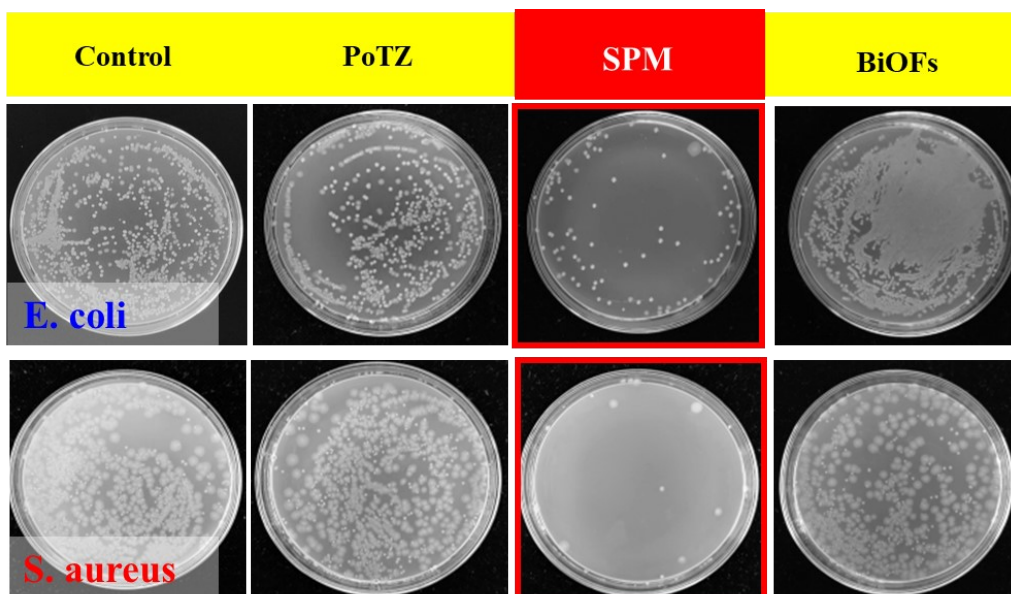


Fig. S10 Antibacterial plate photo of SPM and intermediates (12 h)

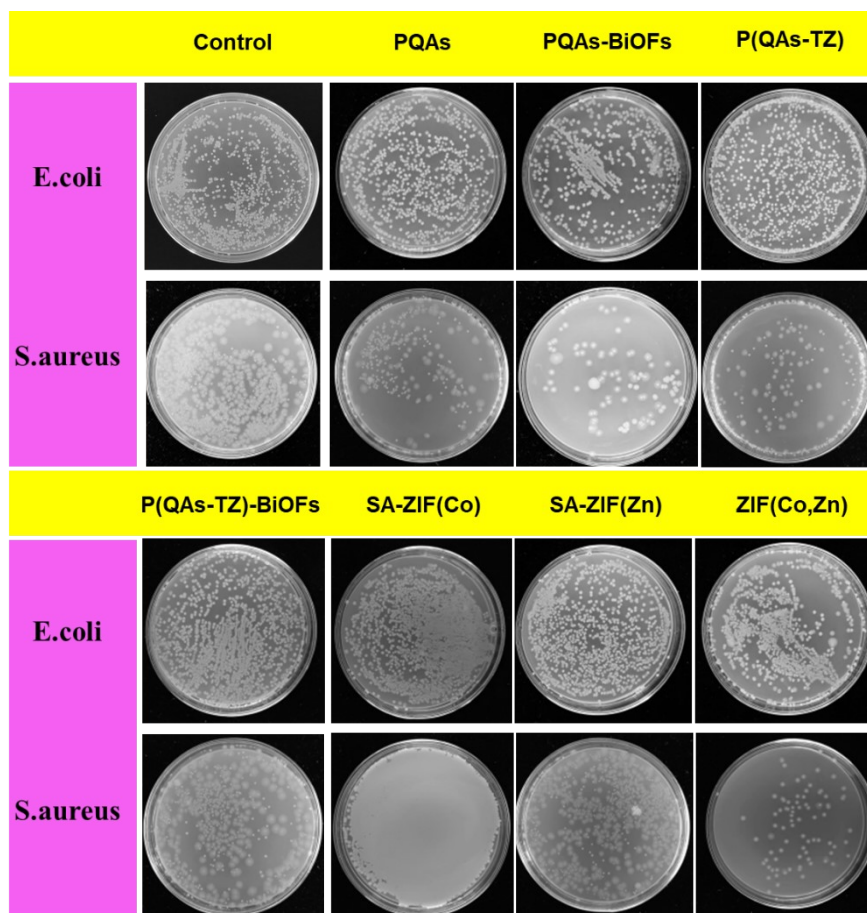


Fig. S11 The digital photograph of antibacterial performance against *E.coli* and *S.aureus* by different materials

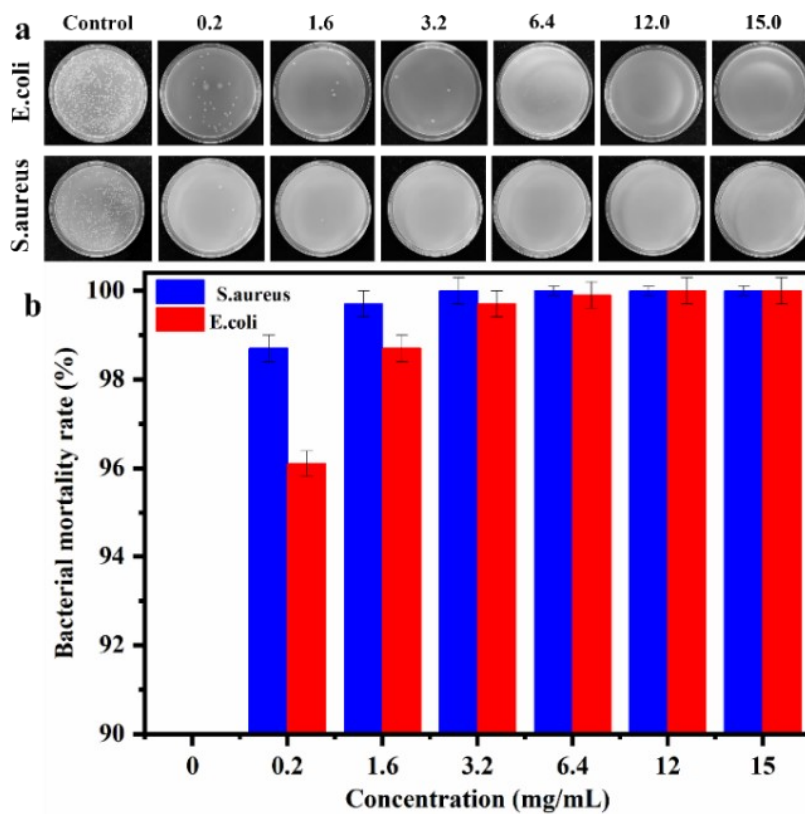


Fig. S12 Digital photographs of *E. coli* and *S. aureus*, after treating with different concentrations of SPM for 12 h (a). Bacterial mortality rate of *E. coli* and *S. aureus* was evaluated with different concentrations of SPM (b).

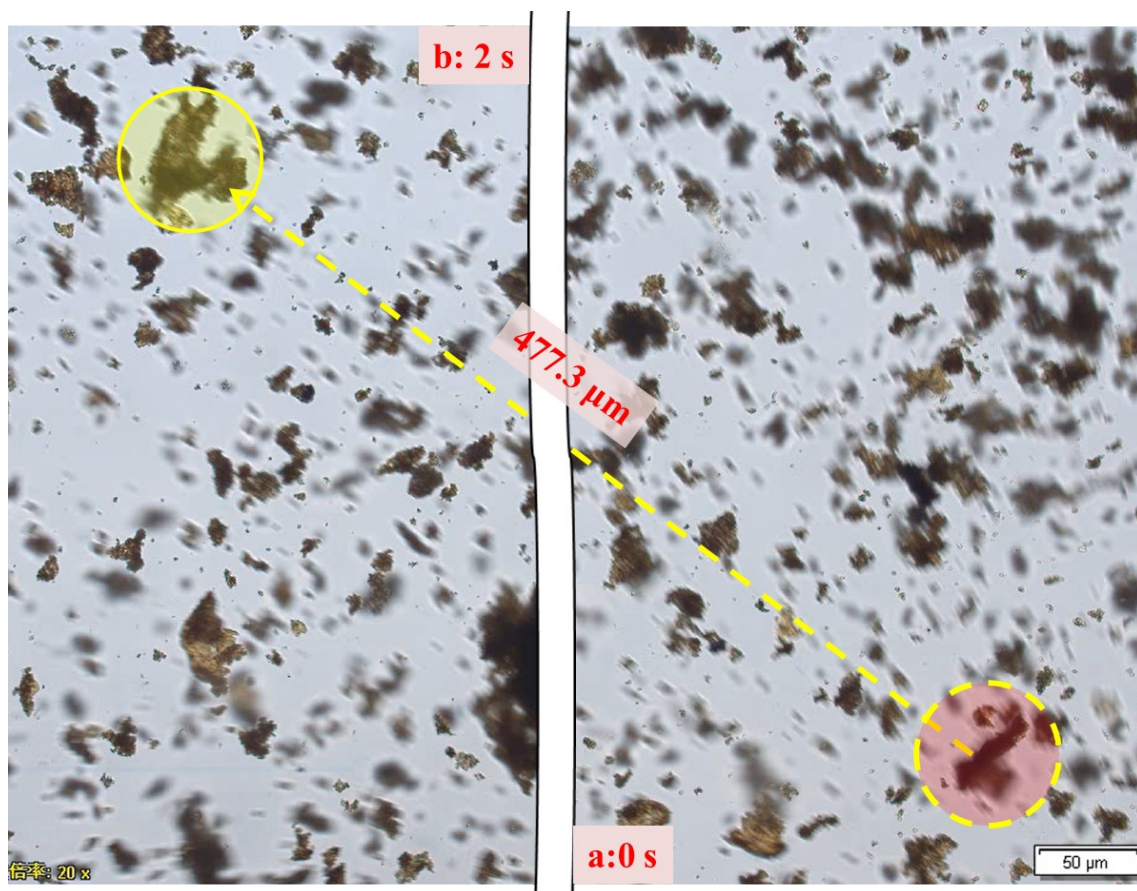


Fig. S13 At the beginning (a) and 2 s (b), the migration of SPM under the light microscope

The specific surface area of SPM was 287.8 m²/g, which was 25 times than that of BiOFs (11.7 m²/g), and 95 times than that of PoTZ (3.0 m²/g). It is mainly due to the formation of polymer chains (PoTZ) in the process of micromotor construction. Therefore, SPM was expected to be able to adsorb pollutant and microorganism. In contrast, the pore size of BiOFs (15.6 nm) was decreased after conjugated with PoTZ (SPM: 13.5 nm). In order to confirm the pore diameter changes of BiOFs, TC (1.4 nm) was selected as a model molecule (Fig. S1). It was indicated that the adsorption capacity of BiOFs (97%) slightly decreased after conjugating with PoTZ (SPM: 85%). It suggests that the monomer of AcTZ was adsorbed into pores of BiOFs before polymerization, and the polymer of PoTZ extended from pore of BiOFs during polymerization process.

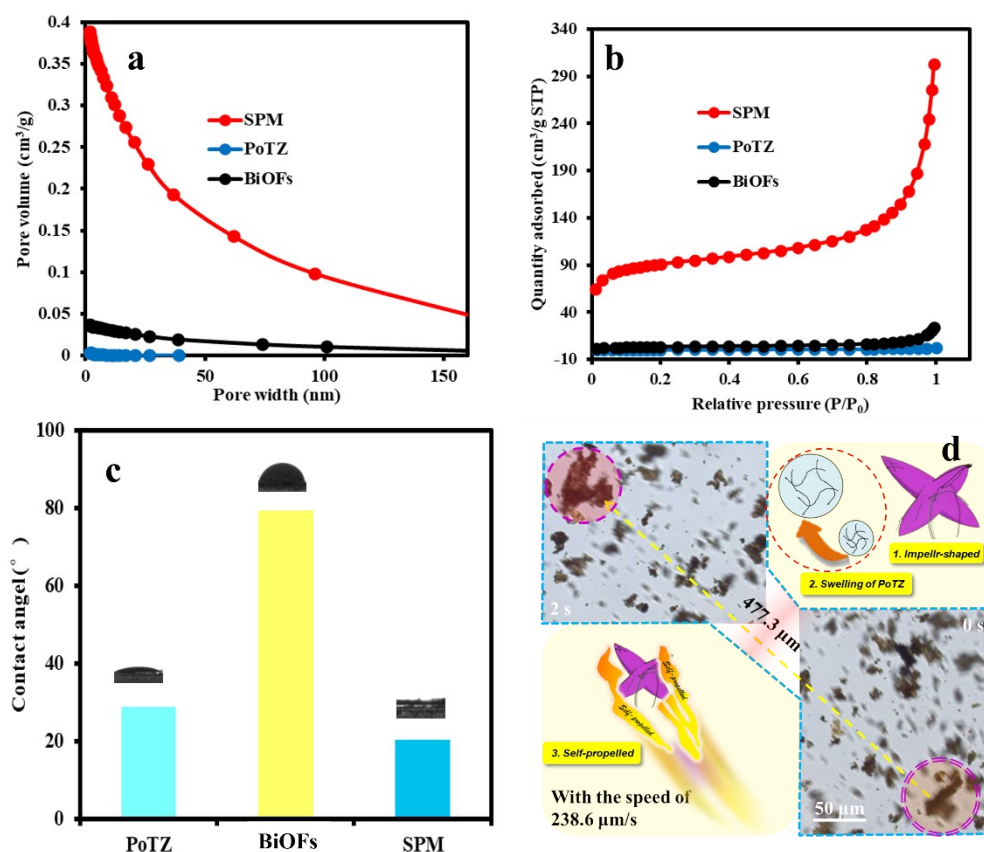


Fig. S14 N₂ adsorption-desorption thermodynamic curves (a) and pore size distribution (b) of BiOFs, PoTZ and SPM; The contact angle of SPM and its intermediate (c); Self-propelled behavior of SPM (d).

Tab. S3 Specific surface area, pore volume and pore size of BiOFs, PoTZ and SPM

Sample	Surface area (m ² /g)	BJH average	Adsorption Pore (cm ³ /g)	volume
PoTZ	3.0171	3.7818	0.0037	
BiOFs	11.7163	15.6108	0.0368	
SPM	287.8501	13.5229	0.3894	

In order to study hydrophilic / hydrophobic performance of SPM, the contact angle was measured, and the results are shown in Fig. S16c. Although BiOFs is relatively hydrophobic (80°) and PoTZ is hydrophilic (29°), their conjugates (SPM) exhibit strong hydrophilicity (20°). It implies the combination of BiOFs and PoTZ effectively improves their hydrophilicity, which enhances the migration of the material in aqueous solution. Furthermore, the migration of SPM in aqueous solution was observed under microscope (Video SI, Fig. S13). Distinctively, SPM moves quickly in water like as self-propelled micromotor, the movement speed of the obtained micromotor (SPM) is able to reach 238.6 $\mu\text{m/s}$ (Fig. S14d). The speed of SPM is faster than that of most kinds of living bacteria. It was hypothesized that the mechanism of micromotor migration came from the swelling of PoTZ in water solution due to the hydrophilicity of SPM. And other aspects may also existence. Therefore, it demonstrated that self-assembly with structure similar to the “Newman projection” and the introduction of polymers allowed SPM to propel quickly and provide the motivation for hunting bacteria.

100 ppm Co^{2+} 5 ppm Co^{2+}



400 mg/L SPM 25 ppm Co^{2+}

Fig. S15 Color rendering detection of Co^{2+} in SPM

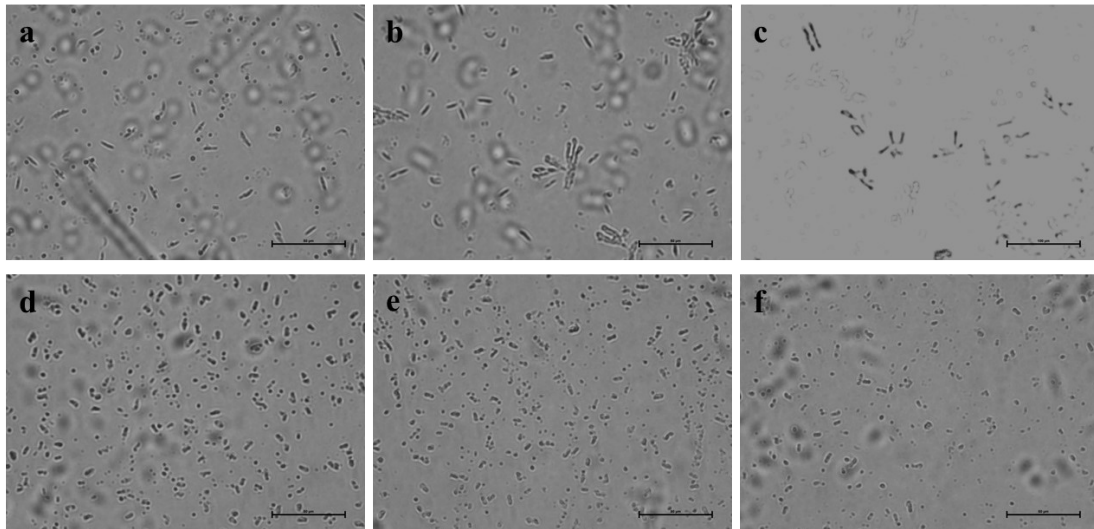


Fig. S16 The adsorption of *E. coli* (a, b, c) and *S. aureus* (d, e, f) by PoTZ, MiBOFs and SPM

Tab. S4 Comparison with reported works

Sample	Propelled (Yes/No)	Antibacterial rate in flowing	MIC E. coli, S. aureus	Cycle, Antibacterial rate (Time,	Ref.
RGO	No	-	0.4 mg/mL, -	-	[S6]
PEM	No	-	2.28 μ mol/mL,	-	[S7]
CoMTT	No	-	0.2 mg/mL, 0.4 mg/mL	-	[S8]
nano-Cu ₂ O/CuO@Ag-tetracycline	No	-	0.15 mg/mL	-	[S9]
SPM	Yes	>90	6.4 mg/mL, 3.2 mg/mL	5, 90	This work

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