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Supporting Information

A nitro-capped tetraaniline derivative with AIE feature for BSA detection and selective imaging of Gram-positive bacteria

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Experimental Section

1.1 Materials and measurements

4,4'-Diaminodiphenylamine sulfate hydrate and diphenyl-acetaldehyde was purchased from TCI Shanghai, 4-fluoronitro-benzene was purchased from Innochem, camphorsulfonic acid was purchased from Adamas. Other reagents were purchased from Beijing Chemical Factory. All reagents and solvents were used without further purification. NMR spectra were completed on a Bruker AV400 spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) and deuterated chloroform (CCl_3D) as solvents at 25 °C. UV-vis absorption spectra were measured on a TU1901 UV-vis spectrometer at room temperature. HR MALDI-TOF MS measurements were carried out on 9.4T Solarix (Bruker). Fourier transform infrared (FTIR) spectra were recorded on a NEXUS-470 spectrometer (Nicolet) using KBr pellet technique. Fluorescence spectra were obtained using F-7000 fluorescence spectrophotometer. Dynamic light scattering (DLS) measurements were performed using Nano ZS90 instrument (Malvern Zetasizer) at room temperature. SEM images were collected on S-4800 scanning electron microscope (Hitachi). Confocal laser scanning microscopy images were collected on a Zeiss laser scanning confocal microscope (LSM7 DUO).

1. 2 Synthesis

Synthesis of N,N''-bis(4''-nitrophenyl)-4,4'-diaminodiphenylamine (**NO_2-Ani_4-NO_2**):

4,4'-Diaminodiphenylamine sulfate hydrate (9.22 g, 31 mmol) and triethylamine (9.95 g, 98 mmol) were dissolved in 50 mL of dimethyl sulfoxide (DMSO) at room temperature, and 4-fluoro-nitrobenzene (11.03 g, 78 mmol) was added in sequence. The mixture was stirred at 90 °C for 72 h under nitrogen atmosphere to avoid the amine oxidation. After the mixture was cooled to room temperature and poured into stirred methanol/water, the resulting precipitation was collected and purified by reprecipitation from tetrahydrofuran (THF) to give desired **NO_2-Ani_4-NO_2** as brown powder (11.62 g, yield 85%). HR MALDI-TOF MS: m/z: 441.143 (M calcd 441.144). FT-IR (KBr, cm^{-1}): 3356 (N-H); 2975, 2913, 2848 (C-H, Ar); 1600, 1297 (NO_2); 1113 (C-N); 831, 750, 694 (C-H, Ar). ^{1}H NMR (400 MHz, DMSO-d_6), δ, ppm: 9.12 (s, 2H, C-NH), 8.22 (s, H, C-NH), 8.04-8.03 (d, 4H, Ar-H), 7.16-7.10 (m, 8H, Ar-H), 6.93-6.90 (d, 4H, Ar-H). ^{13}C NMR (400 MHz, DMSO-d_6), δ, ppm: 152.52, 140.74, 137.45, 132.15, 126.72, 124.07, 118.07, 112.77.

Synthesis of N,N''-bis[(4''-nitrophenyl)-N,N',N''-tris(2,2-diphenyl-vinyl)-4,4'-diaminodiphenylamine (**NO_2-B_3-Ani_4-NO_2**):

NO_2-Ani_4-NO_2 (0.882 g, 2 mmol), camphorsulfonic acid (0.02 g, 0.08 mmol) and diphenyl acetaldehyde (1.177 g, 6 mmol) were dissolved in THF (30 mL), and the resulting mixture was refluxed for 24 h under nitrogen atmosphere with stirring. Then the solvent was removed by rotary evaporation, and the left crude precipitation was purified by recrystallization from ethyl acetate (EA) to give ideal **NO_2-B_3-Ani_4-NO_2** as red powder (1.70 g, yield 87%). HR MALDI-TOF MS: m/z: 975.378 (M calcd 975.378). FT-IR (KBr, cm^{-1}): 3058, 2920, 2853 (C-H, Ar); 1586, 1311 (NO_2); 1502 (C=C); 1113 (C-N); 840, 750, 699, (C-H, Ar). ^{1}H NMR (400 MHz, DMSO-d_6), δ, ppm: 8.09-8.08 (d, 4H, Ar-H), 7.34-7.10 (m, 30H, Ar-H), 6.89-6.86 (m, 8H, Ar-H), 6.80-6.78 (d, 4H, Ar-H), 6.61-6.55 (m, 3H, CH=C). ^{13}C NMR (400 MHz, $CDCl_3$-d_6), δ, ppm: 151.82, 142.80, 140.76, 138.51, 134.94, 130.22-126.95, 126.34, 125.26, 122.95, 117.21.

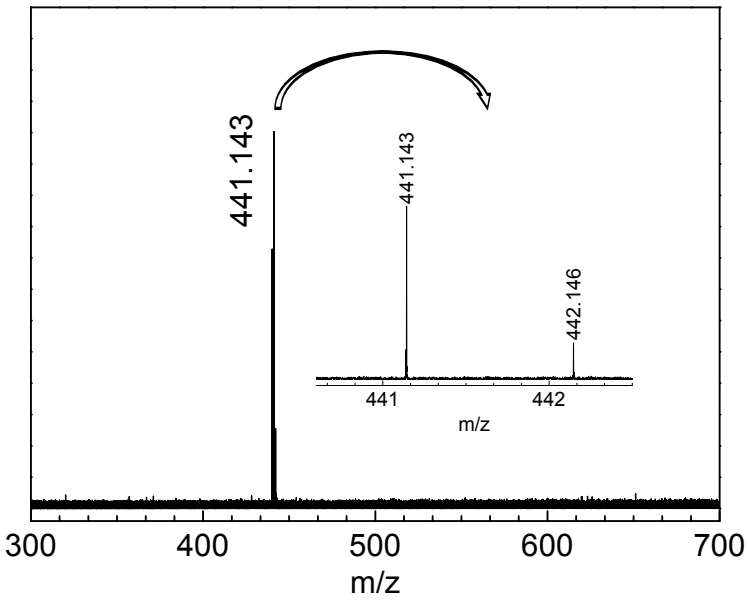


Fig. S1 HR MALDI-TOF MS spectra of **NO_2-Ani_4-NO_2**.

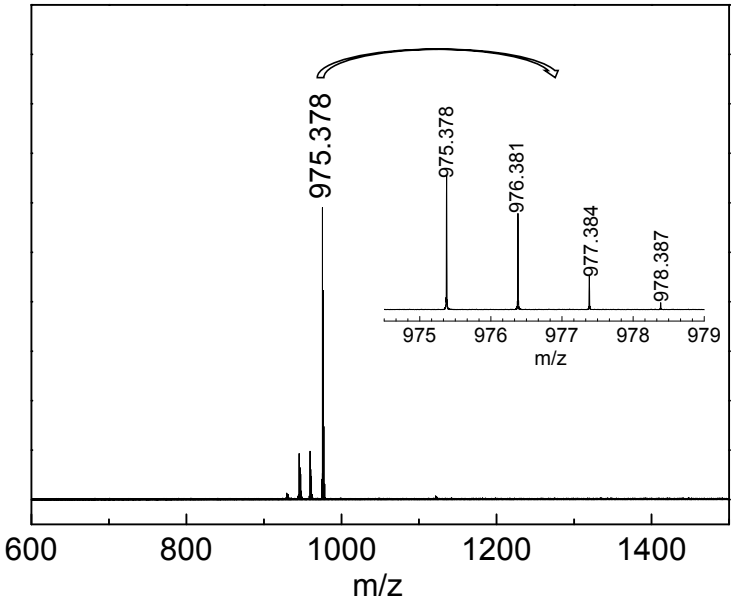


Fig. S2 HR MALDI-TOF MS spectra of **NO_2-B_3-Ani_4-NO_2**.

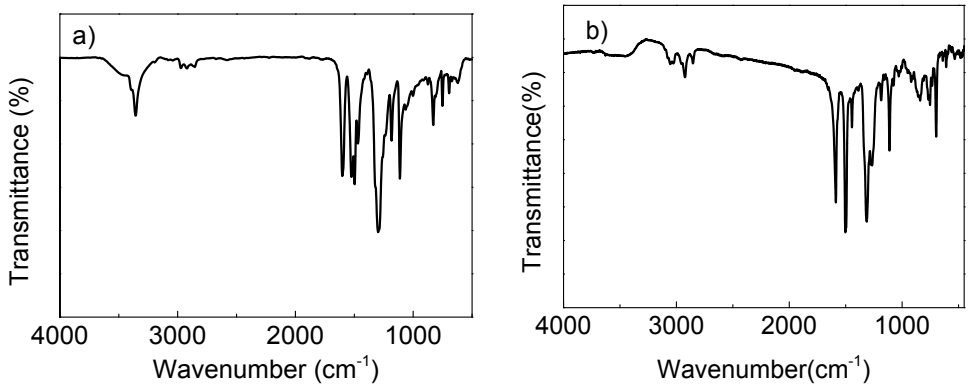
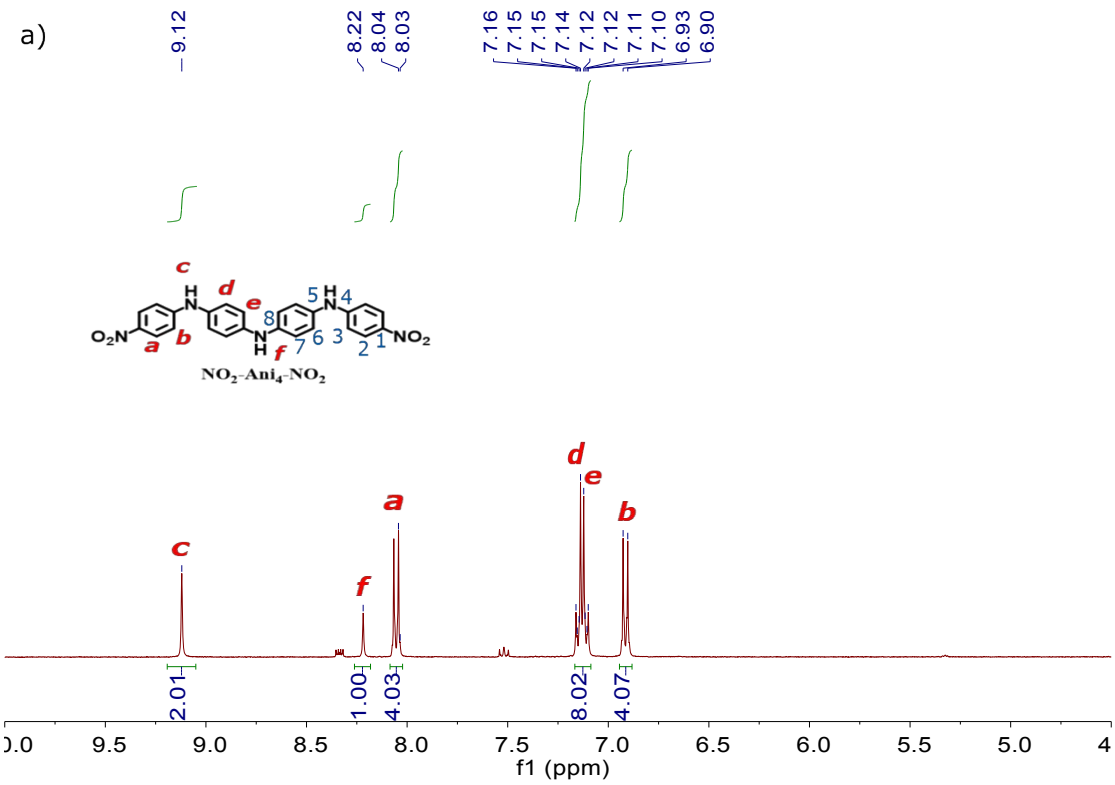


Fig. S3 FT-IR spectra of a) **NO_2-Ani_4-NO_2** and b) **NO_2-B_3-Ani_4-NO_2**.



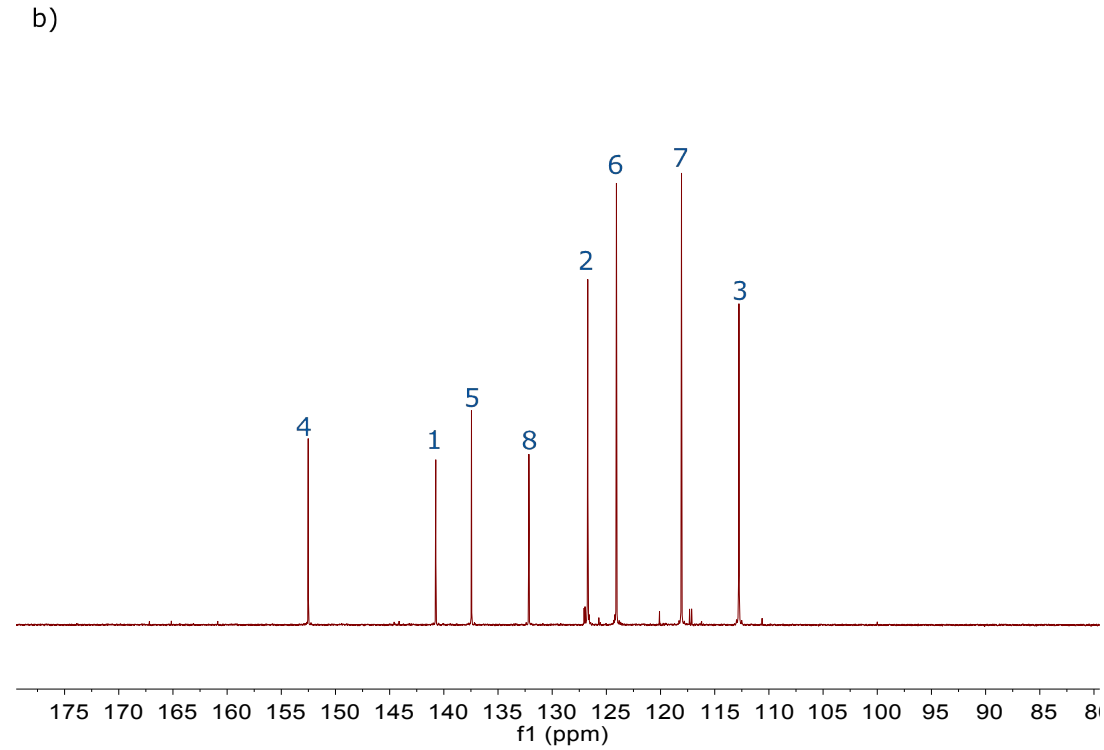


Fig. S4 a) ^{1}H-NMR and b) ^{13}C NMR spectra of **NO_2-Ani_4-NO_2**.

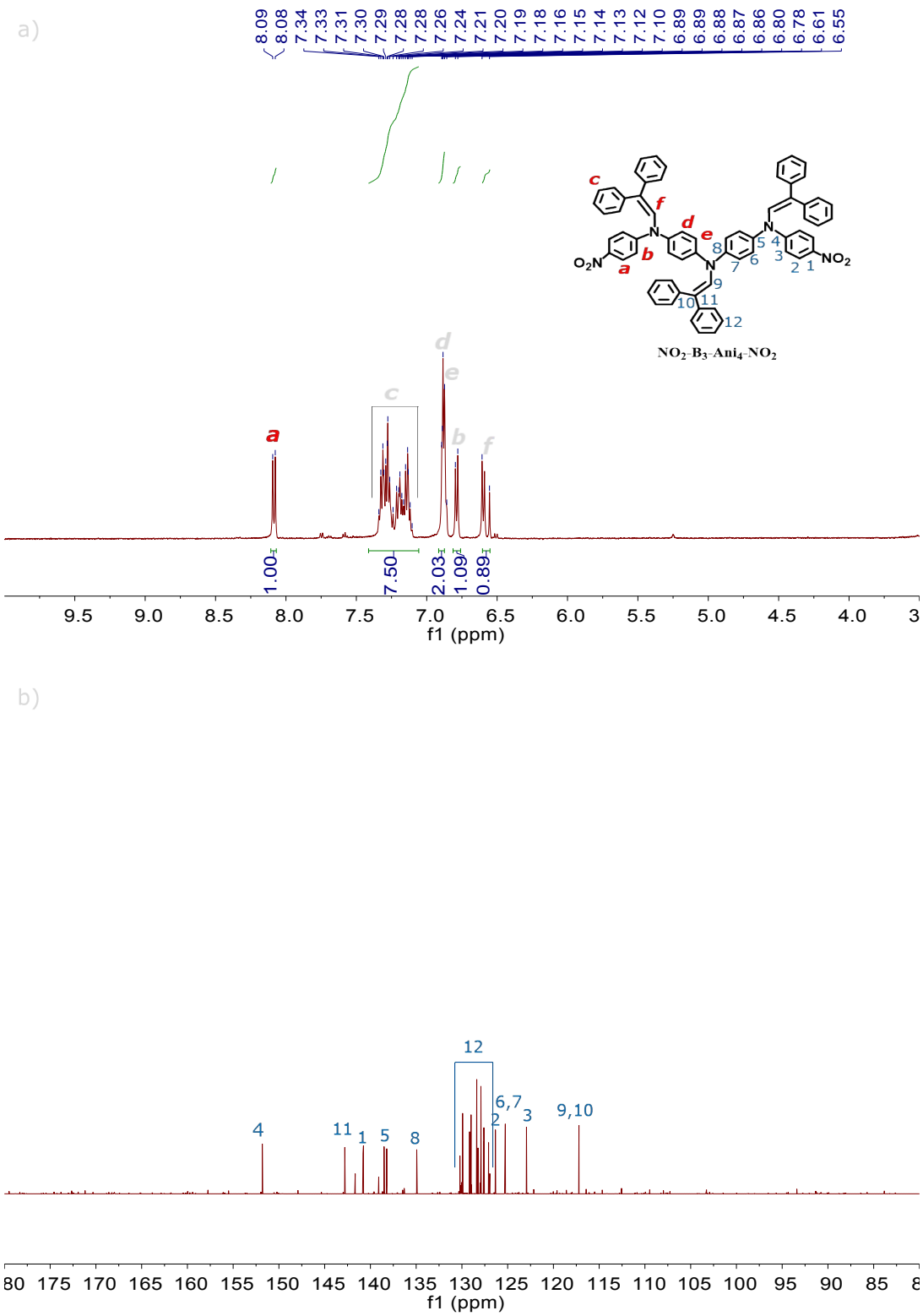
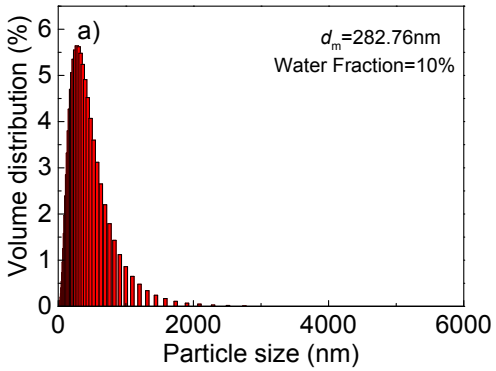
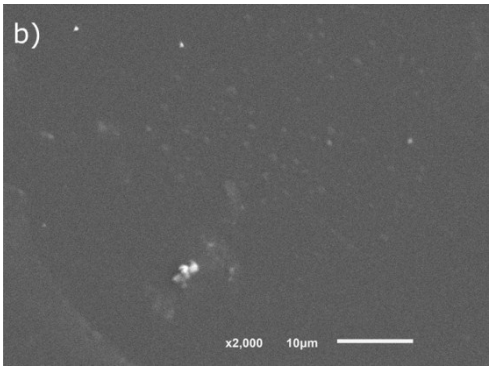
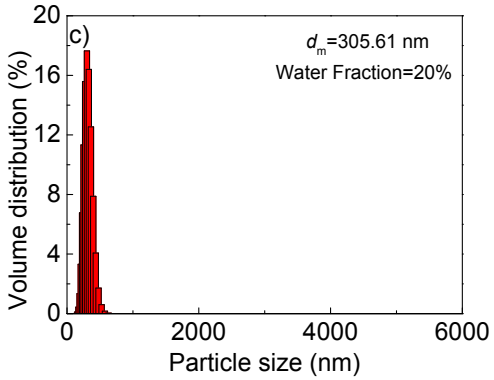
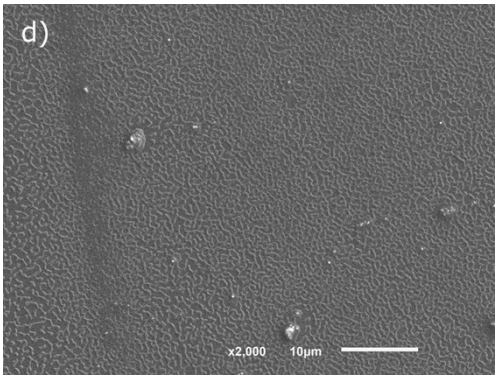


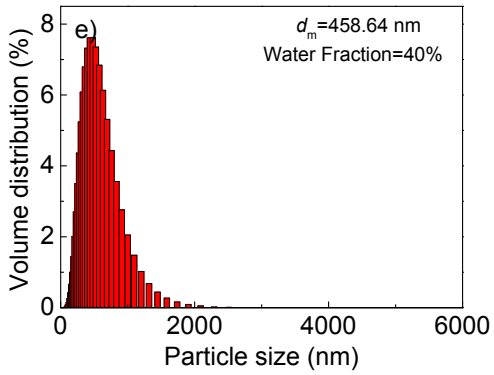
Fig. S5 a) ^{1}H-NMR b) ^{13}C NMR spectra of **NO_2-B_3-Ani_4-NO_2**.

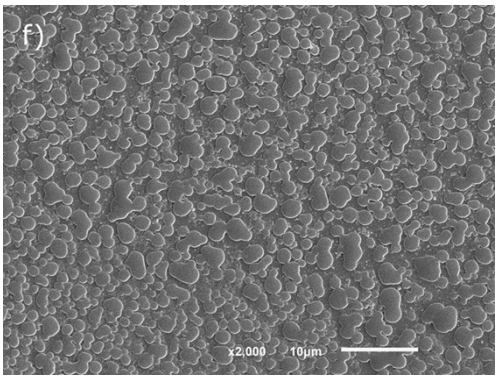

a)
d_m=282.76nm
Water Fraction=10%
Volume distribution (%)
Particle size (nm)

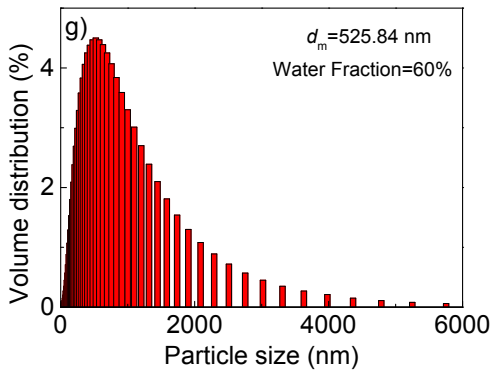

b)
x2,000 10μm

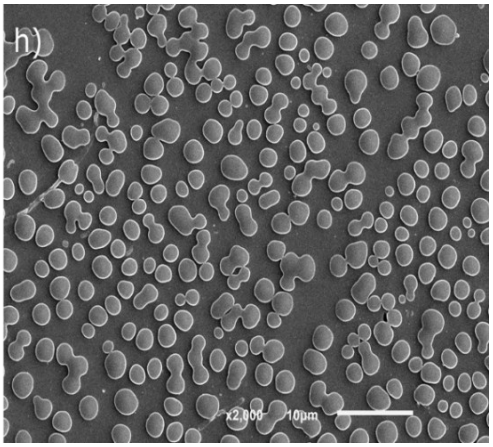

c)
d_m=305.61 nm
Water Fraction=20%
Volume distribution (%)
Particle size (nm)


d)
x2,000 10μm


e)
d_m=458.64 nm
Water Fraction=40%
Volume distribution (%)
Particle size (nm)


f)
x2,000 10μm


g)
d_m=525.84 nm
Water Fraction=60%
Volume distribution (%)
Particle size (nm)


h)
x2,000 10μm

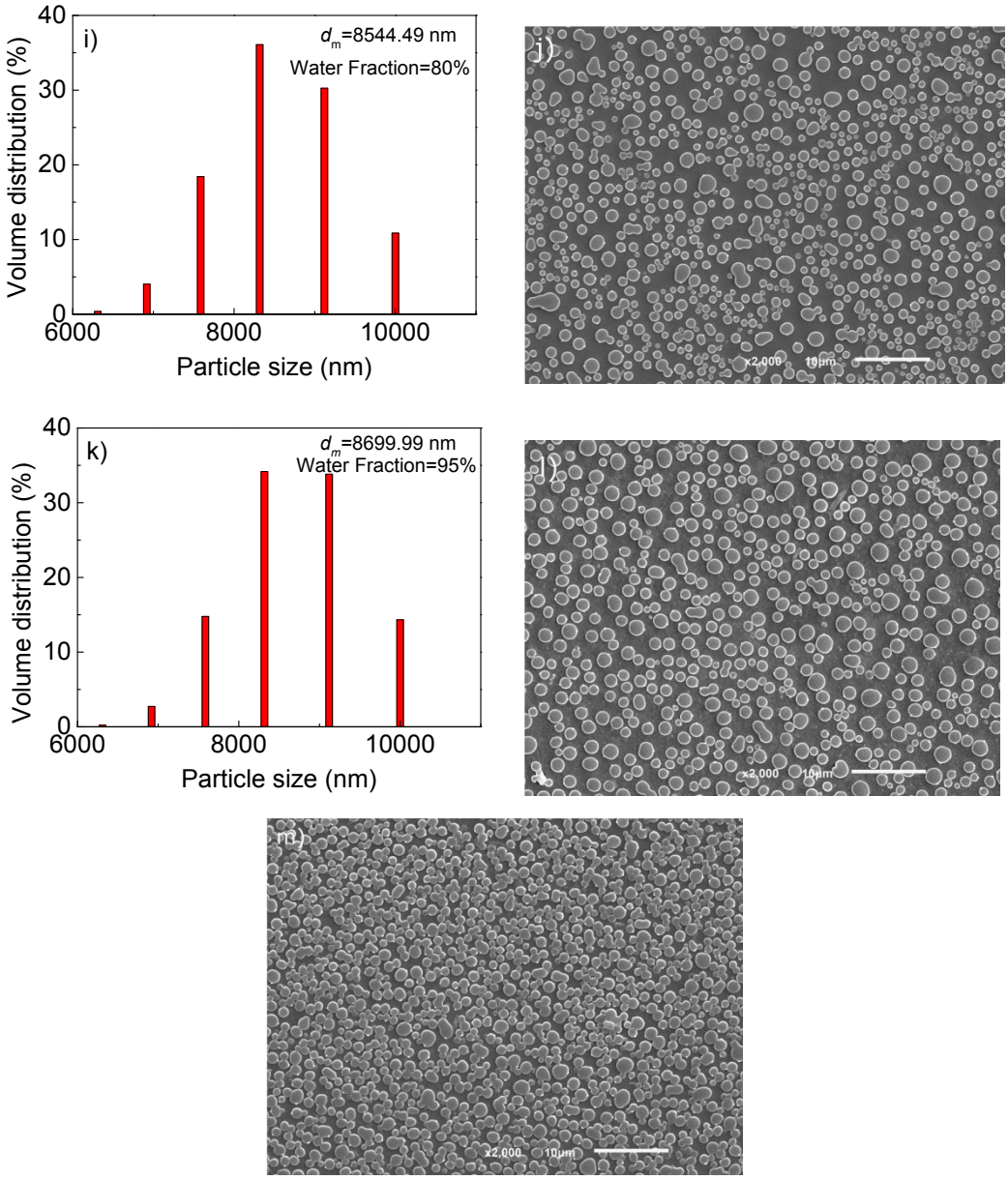


Fig. S6 Particle size distributions (a), c), e), g), i), k) and SEM images (b), d), f), h), j), l), m)) of **NO_2-B_3-Ani_4-NO_2** in DMF/H_2O solution with different water fraction. a), b): v/v, 90/10; c), d): v/v, 80/20; e), f): v/v, 60/40; g), h): v/v, 40/60; i), j): v/v, 20/80; k), l): v/v, 10/90; m): v/v, 5/95.

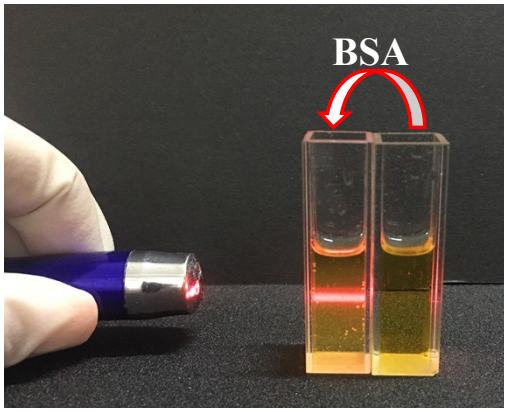


Fig. S7 Photo image for the **NO_2-B_3-Ani_4-NO_2** suspension in DMF/H_2O (v/v, 9:1) with Tyndall effect after the addition of BSA (left) and without Tyndall effect before the addition of BSA (right).

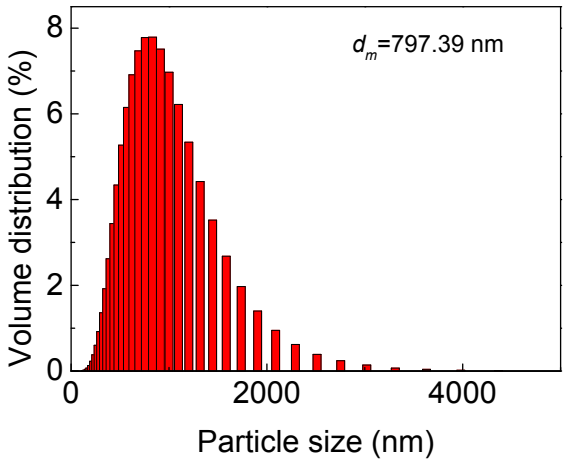


Fig. S8 Particle size distribution of **NO_2-B_3-Ani_4-NO_2** (0.2 μM) in DMF/H_2O solution (v/v, 9/1) after the addition of BSA (100 μg/mL).

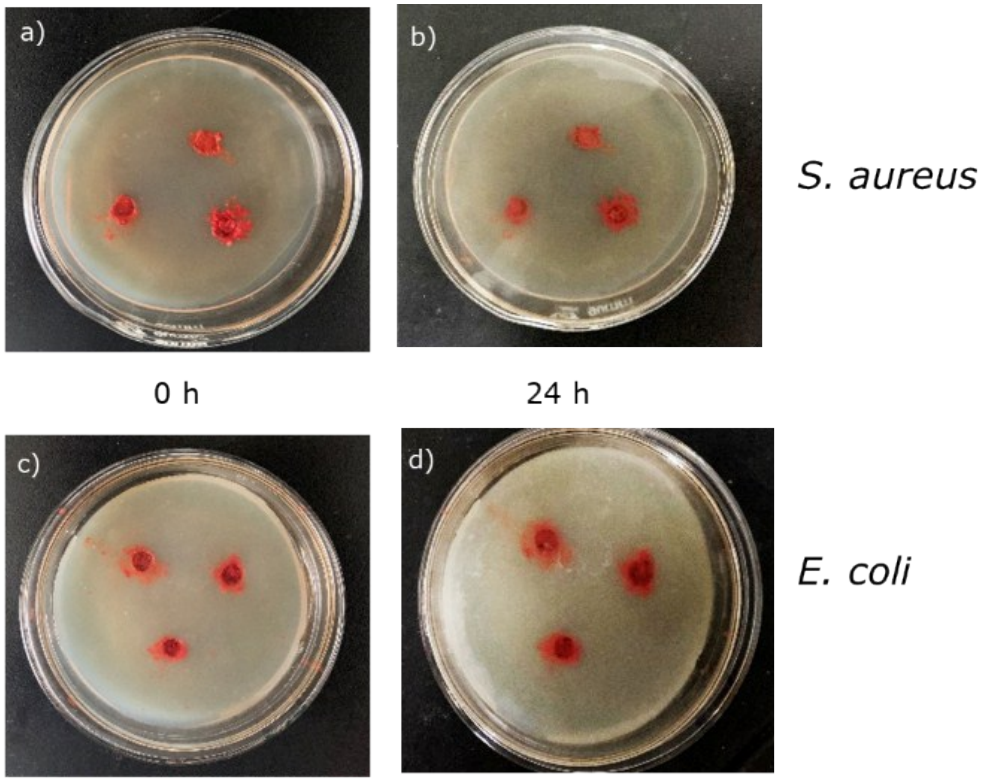


Fig. S9 Effect of **NO_2-B_3-Ani_4-NO_2** on a), b) *S. aureus* and c), d) *E. coli* viability evaluated by inhibition zone method.

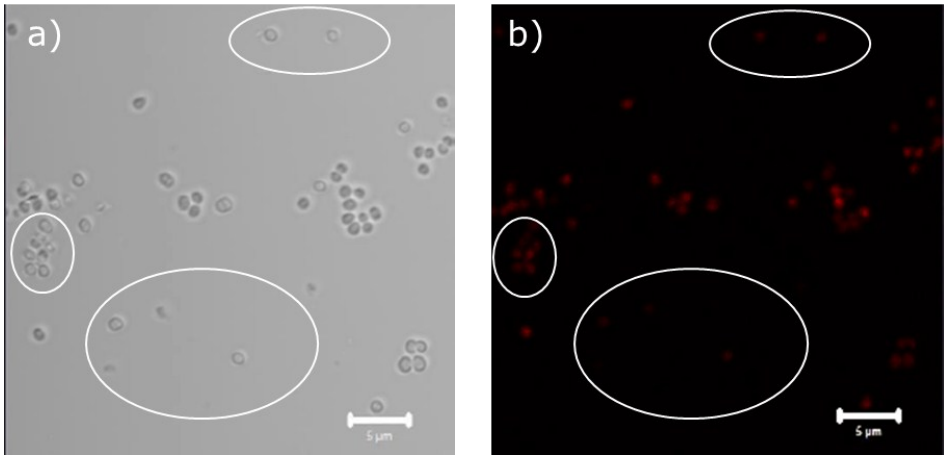


Fig. S10 a) Bright-field and b) fluorescent image of dead *S. aureus* stained with **NO_2-B_3-Ani_4-NO_2** for 30 min. The dead bacteria were treated with 1% trypsin for 24 h before staining. The circles indicate bacteria cell wall.