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Difunctionalized Pillar[5]arene-Based Polymer Nanosheets for Photodynamic Therapy of Staphylococcus aureus Infection

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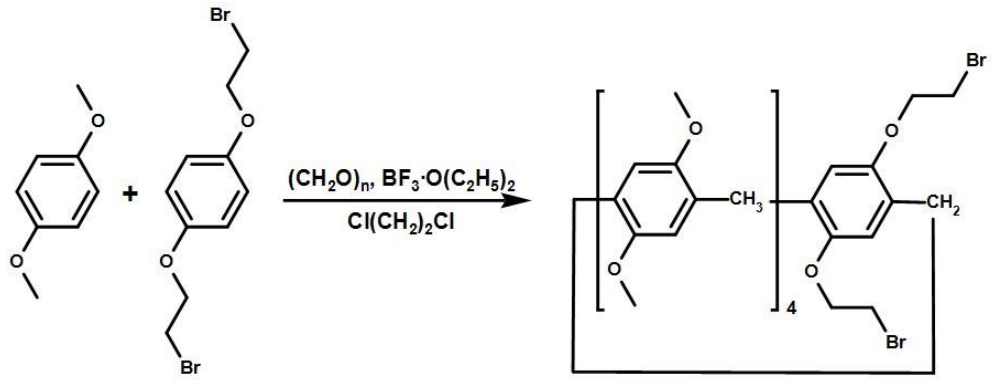
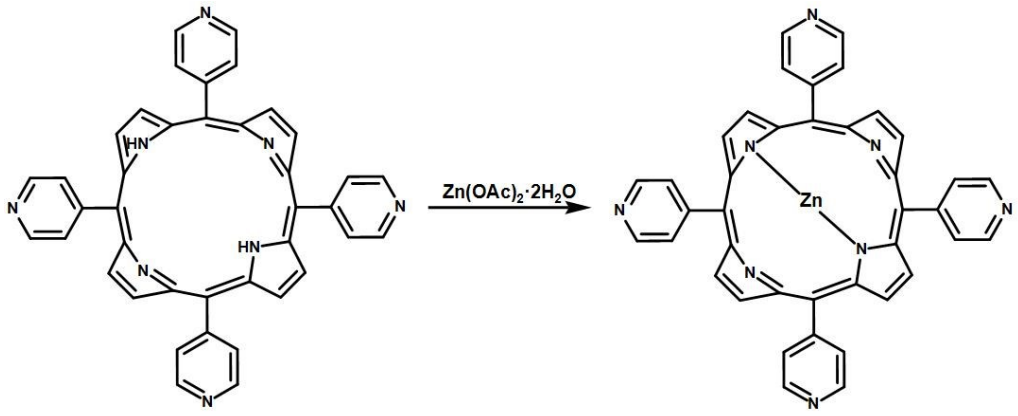
Contents

Materials and Measurements. All the solvents used in the experiments were obtained from Beijing chemical plant. 1,4-Bis-(2-bromo-ethoxy)-benzene, 1,4-dimethoxybenzene, paraformaldehyde boron trifluoride etherate, 5,10,15,20-tetra(4-pyridyl)porphyrin and zinc acetate were purchased from Energy Chemical. DCFH-DA and glutaraldehyde, 2.5% (EM Grade) were purchased from Beijing Solarbio Science & Technology Co., Ltd. (Beijing, China). Dulbecco's modified essential medium (DMEM), fetal bovine serum (FBS) and penicillin-streptomycin solution were obtained from Sangon Biotech (Shanghai) Co., Ltd. The white light used in the experiments was from commercial OPPLE LED bulb lamp. ^{1}H NMR spectra were recorded with a Bruker AVANCE III 500 instrument using a tetramethylsilane (TMS) proton signal as the internal standard. MALDI-TOF tests were performed at the Brucker Autoflex speed TOF/TOF. ζ-potential measurements were conducted with Malvern Instrument Zetasizer Nano ZS90 instrument) at 25 °C. Scanning electron microscopy (SEM) images were captured with a JEOL JSM 6700 F instrument. Transmission electron microscopy (TEM) images were captured with a JEM-2100 F instrument. Atomic force microscopy (AFM) images were captured with a Bruker Dimension Fast Scan Atomic Force Microscopy instrument in tapping mode. UV-vis absorption spectra were performed on a Shimadzu 3100 UV-vis spectrophotometer. Fourier transform infrared (FTIR) spectra were recorded on a Brucker VERTEX 80 V. Fluorescence spectra were recorded on a Shimadzu 5301PC. EPR measurements were conducted on a JEOL JES-FA 200 instrument. CLSM characterization was performed on a ZEISS LSM 710 apparatus. The absorbance for MTT assay analysis was measured on a microplate reader (DeTie HBS-

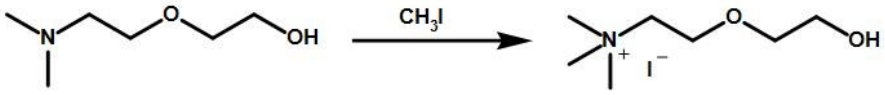
1096B) at the wavelength of 490 nm.



Scheme S1. Synthesis route of 1,4-bis(bromoethyoxy)copillar[5]arene.



Scheme S2. Synthesis route of TPyP-Zn.



Scheme S3. Synthesis route of 2-(2-hydroxyethoxy)-N,N,N-trimethylethanaminium iodide.

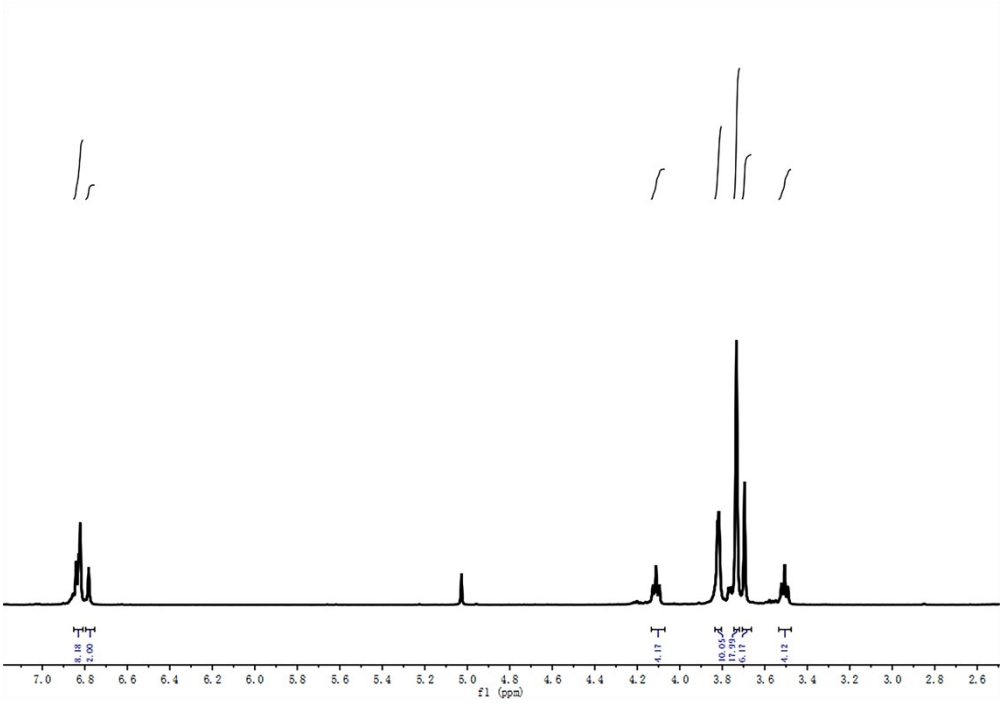


Fig.S1 ^{1}H-NMR spectrum of 1,4-bis(bromoethyoxy)copillar[5]arene. ^{1}H-NMR (500 MHz, $CDCl_3$, 25 ℃, TMS): δ (ppm): 6.82 (t, 8H), 6.78 (s, 2H), 4.11 (t, 4H), 3.82 (s, 10H), 3.73 (s, 18H), 3.69 (s, 6H), 3.51 (t, 4H).

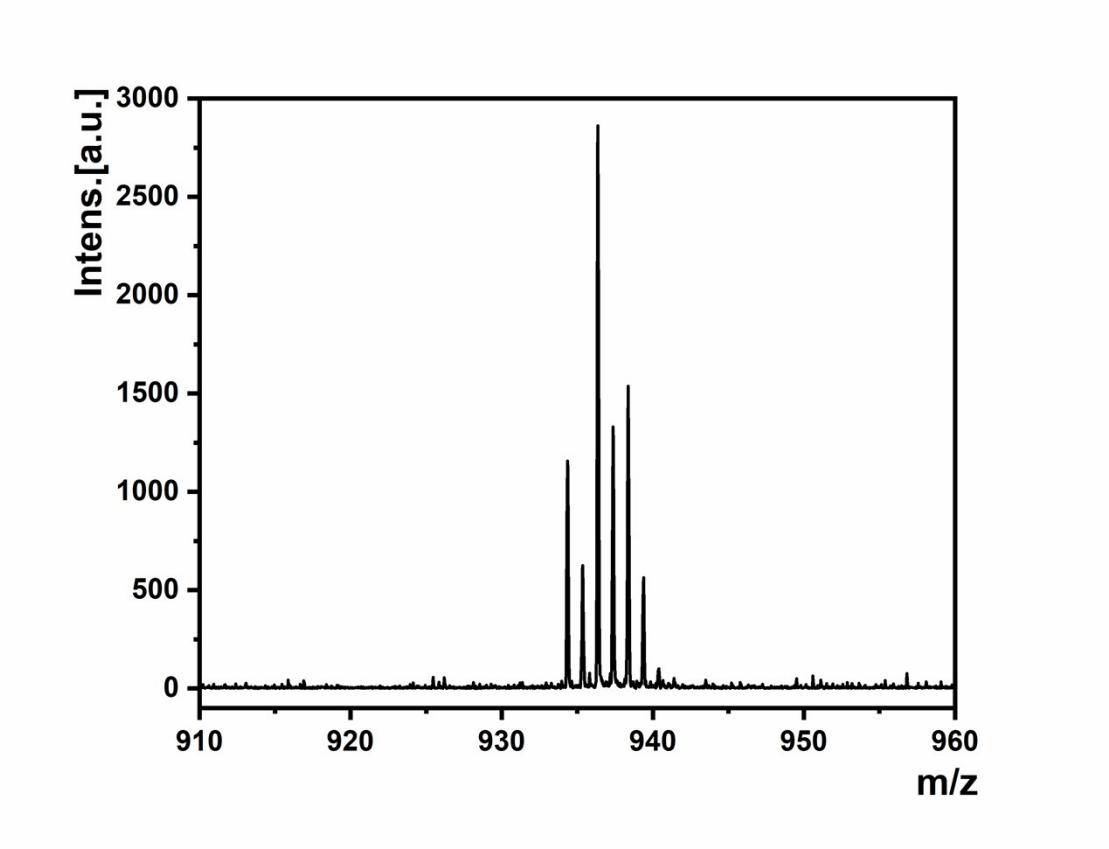


Fig.S2 MALDI-TOF spectrum of 1,4-bis(bromoethyoxy)copillar[5]arene. MS (Maldi-Tof): m/z: 936.36.

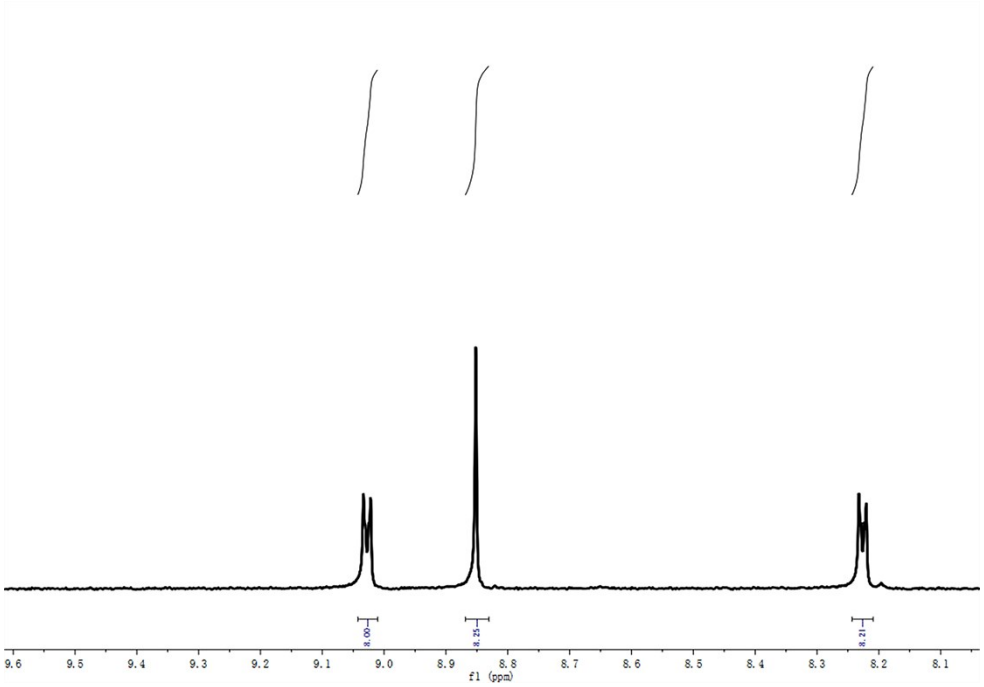


Fig.S3 ^{1}H-NMR spectrum of TPyP-Zn. ^{1}H-NMR (500 MHz, d_6-DMSO, 25 ℃, TMS): δ (ppm): 9.01 (d, 8H), 8.85 (s, 8H), 8.23 (d, 8H).

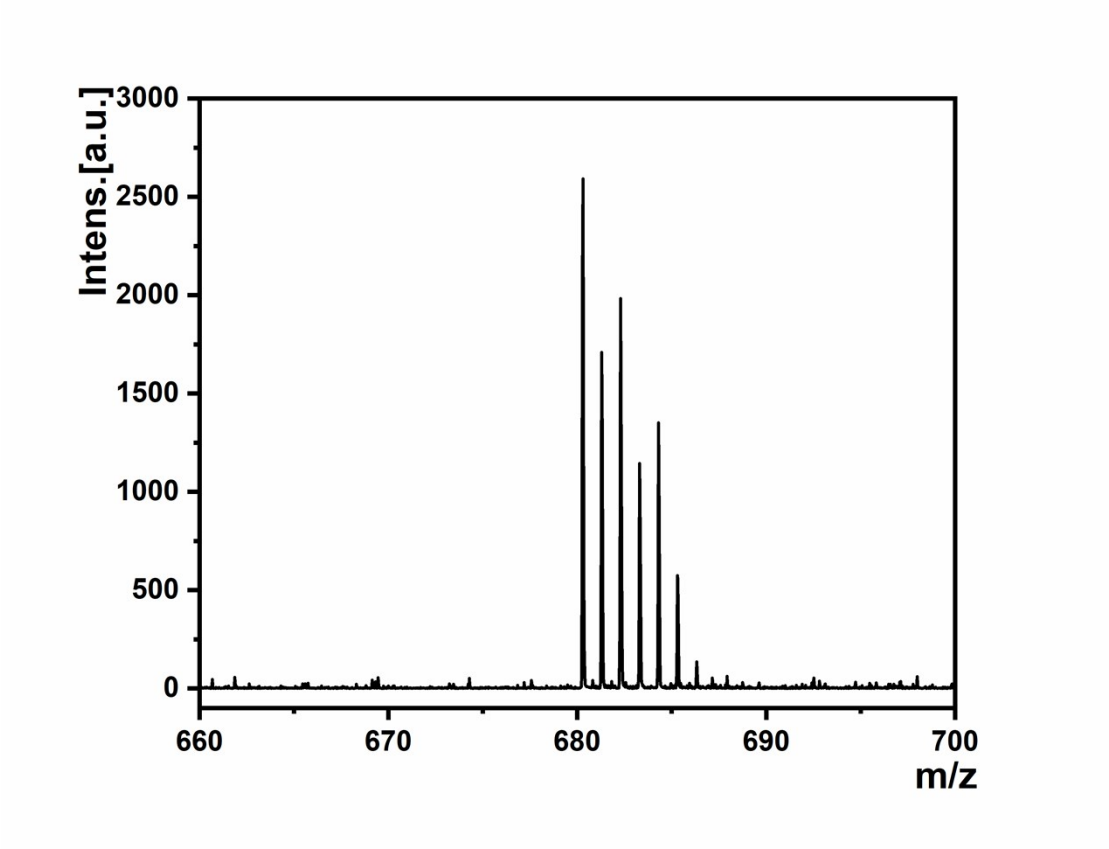


Fig.S4 MALDI-TOF spectrum of TPyP-Zn. MS (Maldi-Tof): m/z: 680.29.

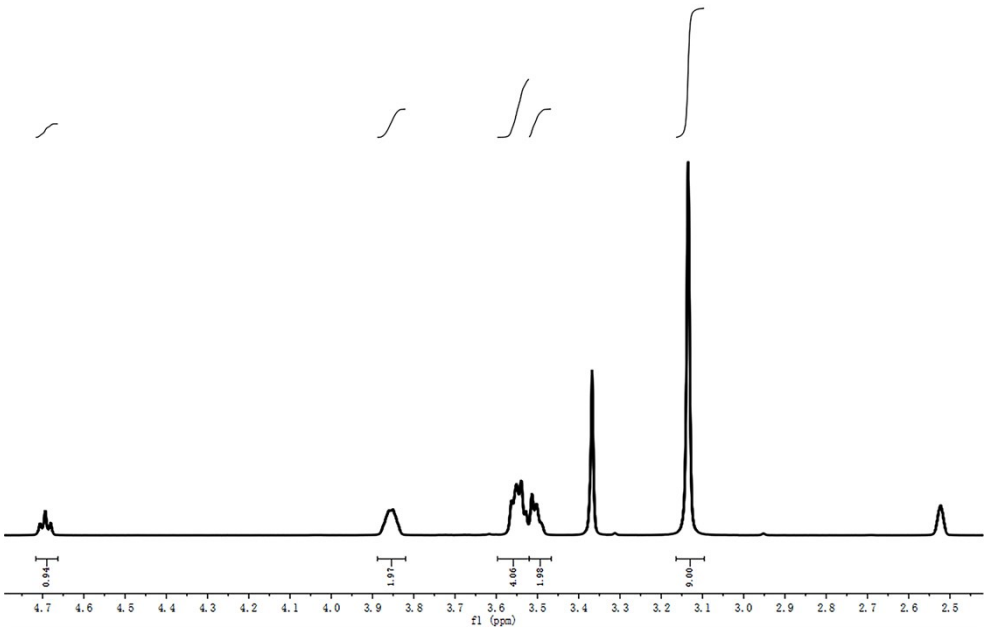


Fig.S5 ^{1}H-NMR spectrum of 2-(2-hydroxyethoxy)-N,N,N-trimethylethanaminium iodide. ^{1}H-NMR (500 MHz, d_6-DMSO, 25 ℃, TMS): δ (ppm): 4.69 (t, 1H), 3.85 (t, 2H), 3.55 (m, 4H), 3.51 (t, 2H), 3.13 (s, 9H).

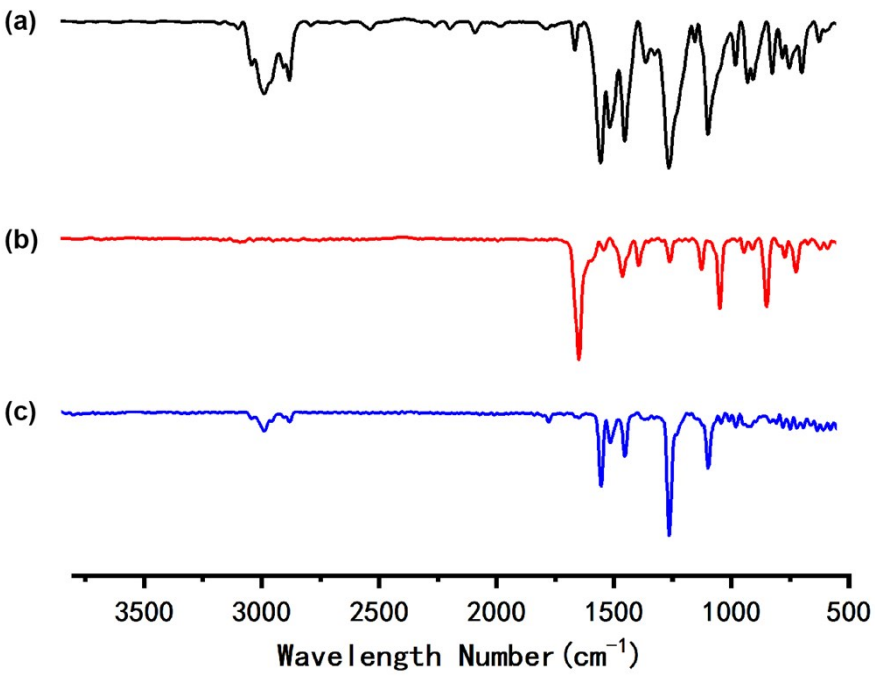


Fig.S6 FTIR spectrum of a) BMCP5; b) TPyP-Zn; c) purified polymer nanosheets.

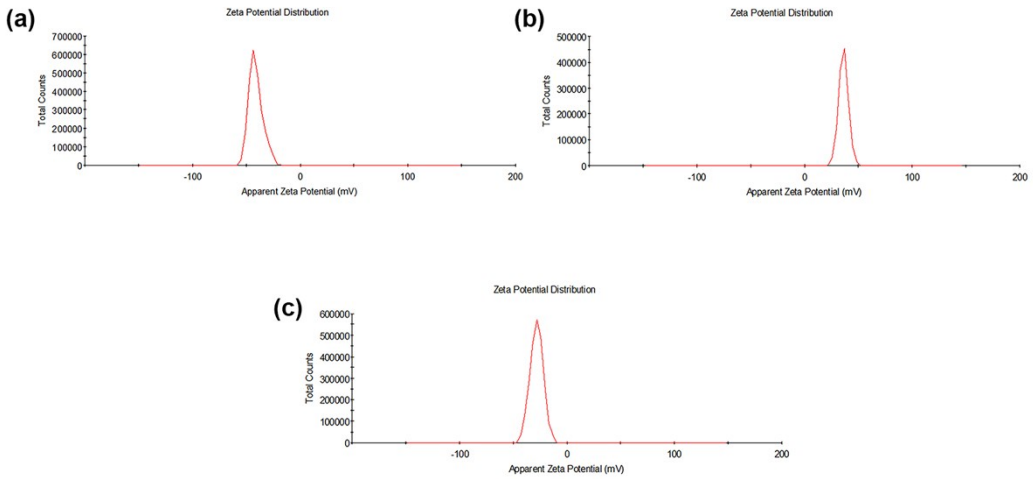


Fig.S7 ζ-Potential of a) *MRSA* (-41.2 mV); b) purified polymer nanosheets (+36.2 mV); c) *MRSA*-nanosheets complex (-28.4 mV).

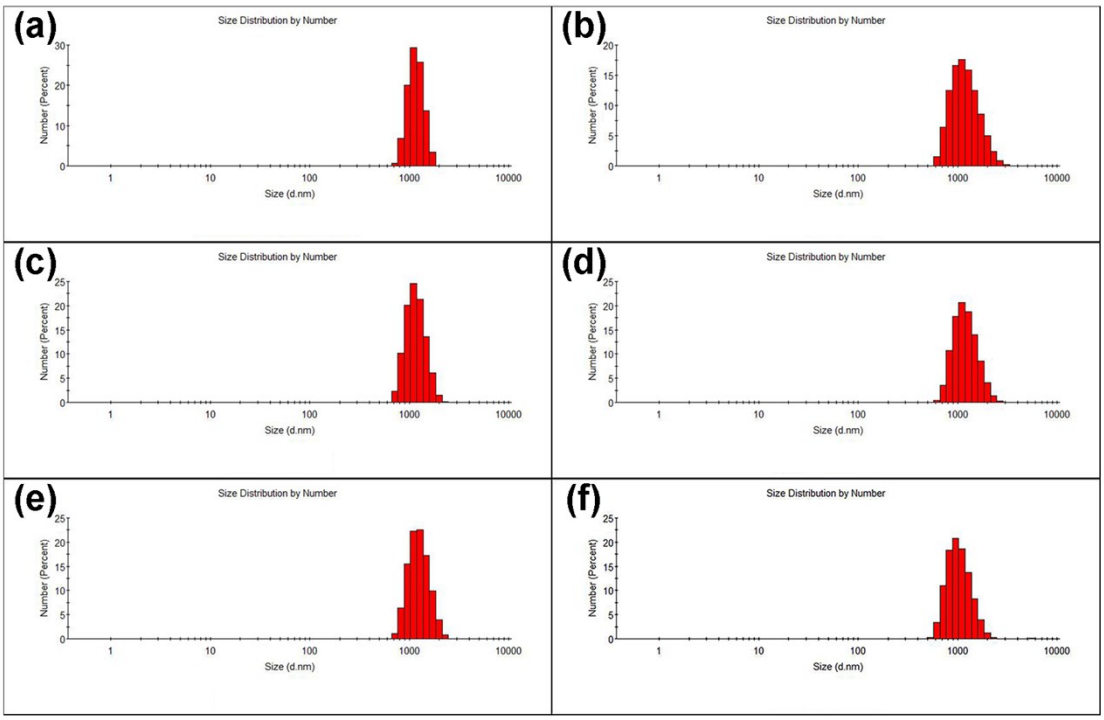


Fig.S8 Hydrodynamic sizes of the nanosheets in PBS measured by DLS. (a), (b), (c), (d), (e), and (f) represent the nanosheets which have stayed for 0, 3, 6, 9, 12 and 24 h.

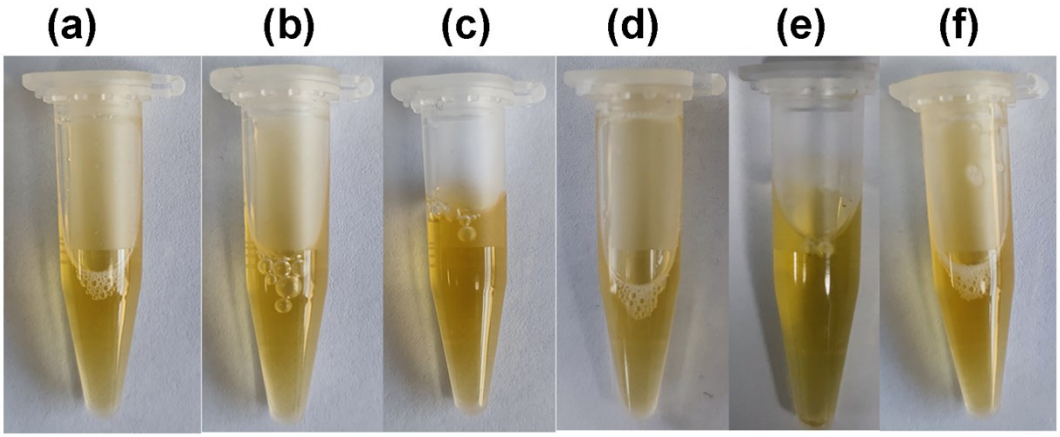


Fig.S9 Pictures of nanosheets in 50% serum at different intervals. (a), (b), (c), (d), (e), and (f) represent the nanosheets which have stayed for 0, 3, 6, 9, 12 and 24 h.