Supporting Information for

ZIF-8 Film Coatings Render Polymeric Device Surfaces Addressable by $^{1}H/^{129}Xe$ MRI

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This file includes:

Supporting text
Figures S1 to S26
Table S1
SI References

Supporting Information Text

Materials and Methods

Synthesis of ZIF-8 powder: The synthesis of ZIF-8 with the assistance of HCOONa followed the literature report [1]. 2-methylimidazole (2-MI, 5.21 g) was dissolved in 40 mL methanol, while $ZnCl_2$ (1.01 g) and HCOONa (1.45 g) were dissolved in another 40 mL methanol. The former solution was poured into the latter solution under vigorous stirring. Then, the mixed solution was transferred into a 100 mL Teflon-lined autoclave, and the autoclave was subsequently heated to 120 °C for 4 h, then cooled to room temperature. The product was collected after centrifugation under 10000 rpm, washed by methanol for 3 times, and dried at 80 °C overnight to yield ZIF-8 powder.

Synthesis of Zn-PDA powder and PDA powder: The synthesis of Zn–polydopamine (Zn-PDA) powder and PDA powder followed the literature report [2, 3]. Dopamine hydrochloride (200 mg) of and $ZnCl_2$ (400 mg) were added into 100 mL Tris-HCl buffer (10 mM, pH 8.5). After stirring at room temperature for 24 h, the product was collected by centrifugation under 8000 rpm and washing with deionized water for 3 times. The Zn-PDA powder was dried under vacuum at 50 °C for 12 h. The PDA powder was prepared by adding 200 mg of dopamine hydrochloride into 100 mL of Tris-HCl buffer (10 mM, pH 8.5), and then stirred, centrifuged and dried in the same manner as Zn-PDA.

Characterization: SEM images were taken from a ZEISS Sigma300 thermal field scanning electron microscopy equipped with an energy dispersive X-ray spectroscopy (EDX, Oxford X-MAX). The ATR-FTIR spectra was recorded on a Thermo Nicolet iS50 IR spectrometer made by Thermo fisher Scientific. XRD was tested by a Bruker AXS D8 Advance powder X-Ray diffractomer. All N_2 adsorption experiments were performed on a Micromeritics 3Flex Gas analyzer. XPS was taken from a Thermo Fisher Scientific ESCALAB 250Xi X-Ray photoelectron spectrometer. The concentration of Zn^{2+} in the leaching solution of an 8 cm ZIF-8@PTFE was obtained by Thermo ICP-OES 7200 (Thermo Fisher, USA).

Hemolysis assay: To assess the hemolysis of ZIF-8@PTFE, blood from BALB/c mice was collected and then centrifuged for 15 min (3000 rpm) to obtain precipitated RBCs and resuspended in normal saline (NS). 200 μL RBCs solution was added into 1 mL normal NS and the ZIF-8@PTFE was placed inside. The ddH_2O and NS groups were used as controls, respectively. All groups were incubated at 37 °C for 4 h and then centrifuged for 15 min (3000 rpm) and photographed. Finally, each supernatant was obtained and the absorbance at 542 nm was measured using the SpectraMax 190 (Molecular Devices, USA). The hemolysis rate was calculated by using the following equation:

$$\text{Hemolysis ratio}\ (\%) = \left(\frac{\mathrm{OD}_{\mathrm{ZIF-8@PTFE}} - \mathrm{OD}_{\mathrm{NS}}}{\mathrm{OD}_{\mathrm{ddH_2O}} - \mathrm{OD}_{\mathrm{NS}}}\right) \times 100\% \quad \text{(S1)}$$

$OD_{ZIF\text{-}8@PTFE}$: Optical density of the supernatant collected from the ZIF-8@PTFE-treated group; OD_{NS}: Optical density of the supernatant from the normal-saline-treated group; OD_{ddH_2O}: Optical density of the supernatant from the deionized-water-treated group.

Whole blood clotting test: To assess the blood clotting index of the ZIF-8@PTFE, fresh blood from BALB/c mice was collected and then mixed with deionized water (positive control), PBS buffer (negative control) and the ZIF-8@PTFE, respectively. All groups were incubated at 37 °C for 90 s and then 10 mL deionized water was gently added into the blood. After standing for 15 minutes, each supernatant was obtained and the absorbance at 541 nm was measured using the SpectraMax 190 (Molecular Devices, USA). The blood clotting index was calculated by using the following equation:

$$\text{Blood clotting index}\ (\%) = \left(\frac{\text{OD}_{\text{sample}}}{\text{OD}_{\text{positive control}}}\right) \times 100\% \quad (S2)$$

OD_{sample}: Optical density of the supernatant from the sample group (normal saline or ZIF-8@PTFE); $OD_{positive\ control}$: Optical density of the supernatant from the deionized-water-treated group.

T_1 relaxation measurements for entrapped-^{129}Xe: A small flip angle pulse sequence was used to measure the apparent T_1 relaxation time of entrapped-^{129}Xe. After hyperpolarized gas mixture was bubbled into the solution for 60 s, a 3 s delay was allowed for bubble collapse. A small flip angle non-selective pulse (flip angle = 28.3°) was then applied to the sample, and a free induction decay (FID) was collected immediately after the pulse. The signal was allowed to a 31 s decay before applying another small flip angle pulse to the remaining magnetization, followed by the collection of another FID. This process was repeated for the desired number of points along the decay curve.

In vitro HP ^{129}Xe NMR/MRI: In vitro ^{129}Xe NMR/MRI experiments were performed on a Bruker Avance 400 MHz wide-bore spectrometer (Bruker Biospin, Ettlingen, Germany) using a 10 mm dual-tuned ^{1}H/^{129}Xe volume coil. HP ^{129}Xe was generated by spin-exchange optical pumping (SEOP) with a commercial polarizer (verImagin Healthcare, Wuhan, China). The gas mixture (10% N_2, 88% He, 2% Xe, 26.4% natural ^{129}Xe abundance) was polarized at 398 K and 48 psi and delivered at 0.1 standard L/min through four fused-silica capillaries into the 10 mm NMR tube.

For NMR spectra, gas was bubbled through the tube for 60 s, followed by a 3 s delay to allow bubble collapse. A single-pulse ZG sequence (p1 = 31.8 μs) was applied.

For MRI, images were acquired with a 2D rapid acquisition with relaxation enhancement (RARE) sequence. Representative parameters included:

- **Axial plane:** slice thickness = 10 mm, matrix = 64 × 64, FOV = 30 × 30 mm², bandwidth = 10.8 kHz, TE = 3.9 ms, TR = 56.8 ms, rare factor = 14.
- **Sagittal plane:** slice thickness = 3 mm, matrix = 32 × 32, FOV = 60 × 60 mm², bandwidth = 10.8 kHz, TE = 2.8 ms, TR = 30 ms, rare factor = 8.

For each excitation, xenon bubbling lasted 20 s followed by a 3 s delay before acquisition. The same configuration was used in the endovascular simulator experiments, except that the peristaltic pump remained active to circulate model fluid during acquisition.

In vitro ^{1}H MRI: ^{1}H MRI was carried out on the same Bruker Avance 400 MHz spectrometer with a 10 mm dual-tuned ^{1}H/^{129}Xe volume coil. RARE sequence parameters were:

- **Axial plane:** slice thickness = 10 mm, matrix = 256 × 256, FOV = 30 × 30 mm², bandwidth = 2.0 kHz, TE = 16.3 ms, TR = 1500 ms, rare factor = 8.
- **Sagittal plane:** slice thickness = 3 mm, matrix = 256 × 256, FOV = 60 × 60 mm², bandwidth = 2.0 kHz, TE = 16.3 ms, TR = 1500 ms, rare factor = 8.

Preparation of model fluid: Model fluid was prepared by mixing 40% (v/v) glycerol in 60% (v/v) saline at 37 °C. $CaCl_2$ (3×10^{-3} M) was added into the model fluid, and finally the viscosity of the model fluid was approximately 3 mPa·s [4].

^{129}Xe NMR/MRI and ^{1}H MRI of ZIF-8@PTFE in the rat trachea: In vivo experiments were conducted on female Sprague–Dawley rats (~200 g) using a 7 T animal MRI scanner (Bruker Biospec 70/20 USR, Billerica, MA) with a custom-built dual-tuned birdcage coil. Due to airway dimensions, a thin ZIF-8@PTFE segment (diameter 0.85 mm) was used. Rats underwent tracheostomy, were positioned supine, and ventilated alternately with HP ^{129}Xe and oxygen via a custom MRI-compatible gas-delivery system with real-time pressure monitoring and trigger output.

- **^{129}Xe NMR:** single-pulse acquisition, TR = 48.155 ms, NS = 1, excitation bandwidth = 12.8 kHz, spectral width = 25 kHz.
- **^{129}Xe MRI (lung):** Fast low-angle shot (FLASH) sequence, TR/TE = 24.1/2.5 ms, NS = 1, flip angle = 12°, slice thickness = 40 mm, FOV = 70 × 70 mm², matrix = 128 × 128, excitation bandwidth = 10 kHz, receiving bandwidth = 29.8 kHz.
- **^{129}Xe MRI (ZIF-8@PTFE):** FLASH sequence, TR/TE = 40/2.9 ms, NS = 1, flip angle = 12°, slice thickness = 40 mm, FOV = 70 × 70 mm², matrix = 128 × 128, excitation bandwidth = 3 kHz, receiving bandwidth = 50 kHz.
- **^{1}H MRI:** 2D RARE, TR/TE = 1300/16.9 ms, matrix = 128 × 128, FOV = 70 × 70 mm², slice thickness = 40 mm, NS = 8, rare factor = 8.

^{1}H MRI of ZIF-8@PTFE in the mouse liver: ^{1}H MRI was performed on a BALB/c mouse cadaver (female, 10 weeks) using the 7 T system with a 72 mm ^{1}H volume coil. The thick (diameter 1.34 mm) ZIF-8@PTFE segment was inserted into the liver prior to imaging. A RARE sequence was used with parameters: TR/TE = 1300/18 ms, slice thickness = 2 mm, 7 slices, FOV = 30 × 30 mm², matrix = 256 × 256, NS = 4, rare factor = 4

Radiofrequency (RF) induced heating Experiment: RF-induced heating performance of the ZIF-8@PTFE and the nitinol guidewire (Equipped with a solenoid coil to replicate the active guidewire structure) was tested using a 3 T human MRI scanner (uMR 780 [Xe]; verImagin Healthcare, Wuhan, China). A continuous balanced steady state free precession (bSSFP) sequence (TE/TR: 1.98/4.79 ms, flip angle: 75°, FOV: 320 × 320 mm, bandwidth: 300 Hz/Px, matrix: 192 × 75, slice thickness: 6 mm) was used. MRI scans were performed in the “First Level” specific absorption ratio (SAR) mode (3.8798 W/kg). IRADIMED 3885T (IRadimed Corporation, USA) equipped with a fiberoptic temperature probe was used for temperature measurements. The fiberoptic temperature probe was tightly secured to the active guidewire or the ZIF-8@PTFE. MRI scans lasted for 17 min, with the temperature recorded every 30 s.

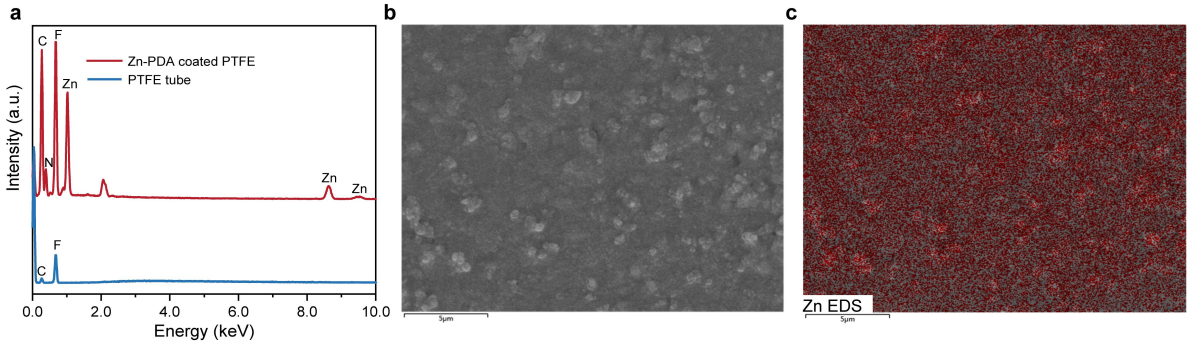

Figure S1. (a) EDX spectrum. (b) SEM image of Zn-PDA coated PTFE. (c) Elemental mapping of Zn corresponding to (b).

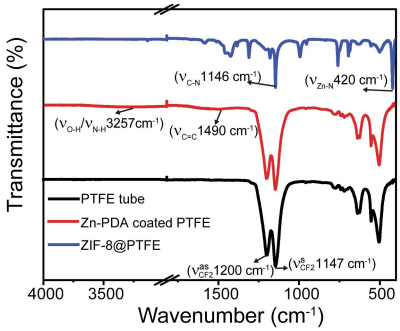

Figure S2. ATR-FTIR analysis of pristine PTFE tube, Zn-PDA coated PTFE and ZIF-8@PTFE.

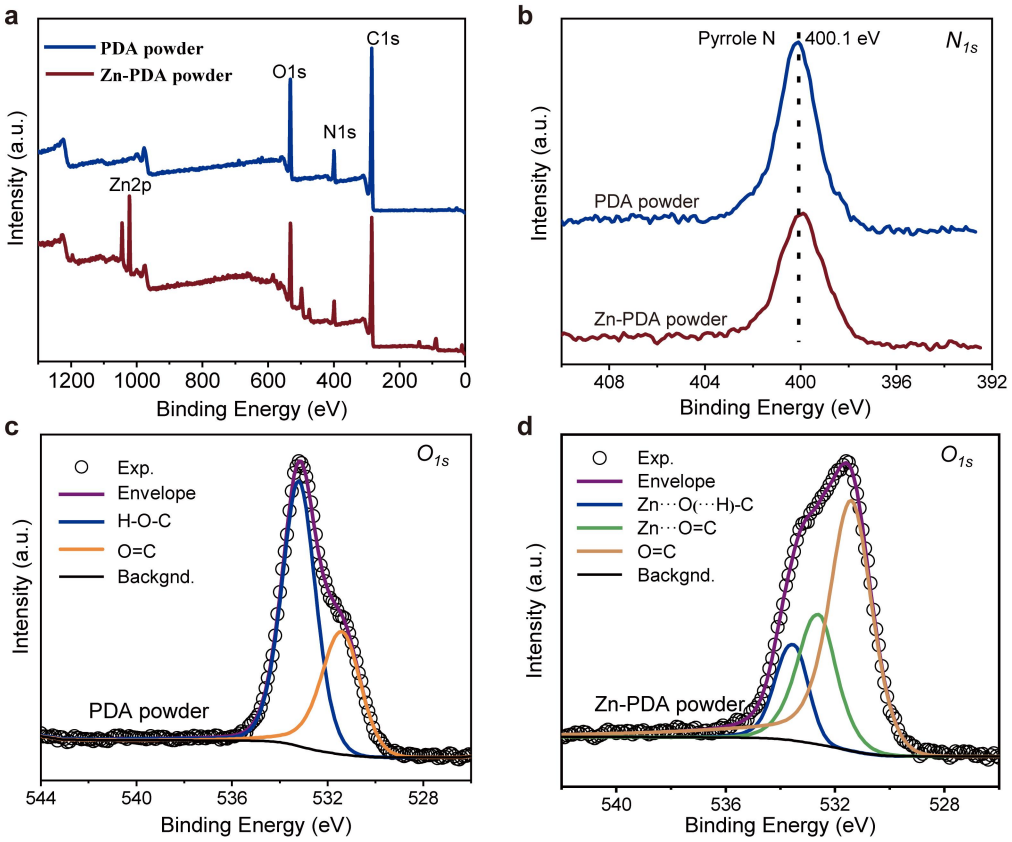

Figure S3. (a) XPS survey spectra of PDA powder and Zn-PDA powder. (b) N1s XPS spectra of samples corresponding to a. O1s XPS spectra of (c) PDA powder and (d) Zn-PDA powder. The high-resolution spectra of O1s of PDA and Zn-PDA powder are shown in Figure. S3c and Figure. S3d respectively, Zn-PDA powder shows three components at 531.41, 532.60, and 533.52 eV assigned to O=C, Zn···O=C, and Zn···O(···H)-C bonds, respectively. In comparison, PDA powder shows only two components at 531.41 and 533.21 eV assigned to O=C and O-C bonds, indicating that Zn(II) ions coordinate with oxygen atoms on the catechol or benzoquinone in mono or bi dentate-fashion [2]. Furthermore, N1s XPS spectra of all samples exhibits a single and narrow symmetric peak, indicating that there is hardly any co-ordination bond formed between Zn(II) and nitrogen atoms in Zn-PDA powder [2] (Figure. S3b).

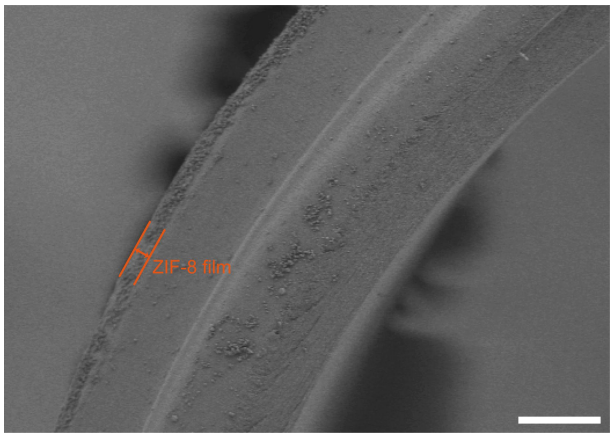

Figure S4. SEM image of the cross section of the ZIF-8@PTFE. A uniform ZIF-8 film with thickness of ~8 μm is clearly observed (scale bar: 40 μm).

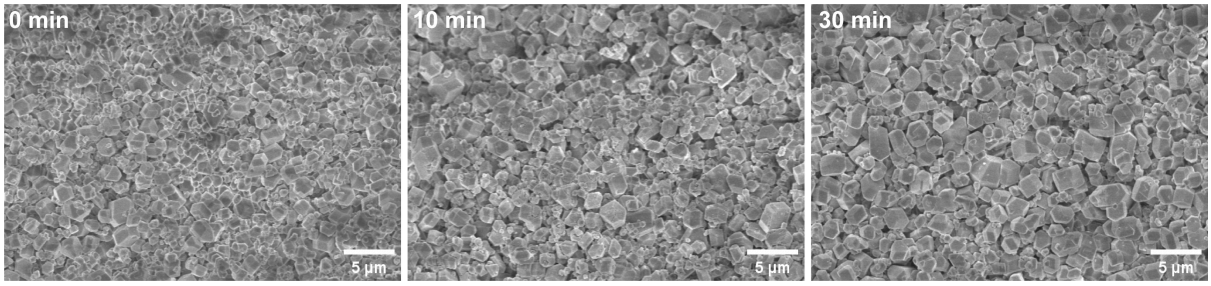

Figure S5. SEM images of the ZIF-8@PTFE surface after immersion in aqueous solution.

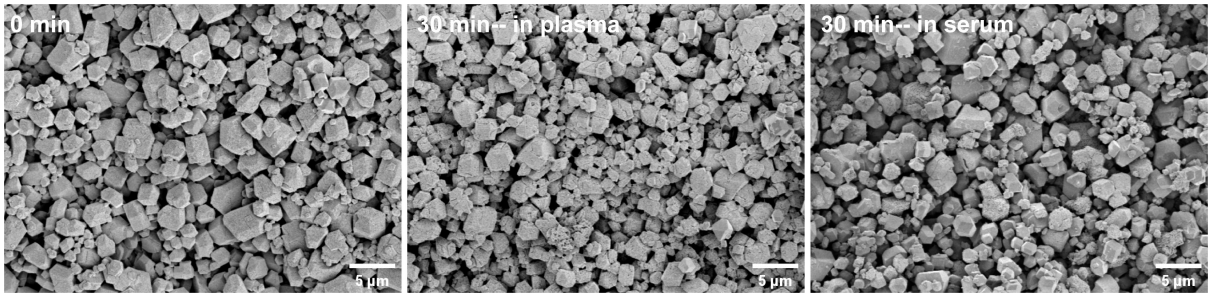

Figure S6. SEM images of ZIF-8@PTFE surface after immersion in plasma/serum.

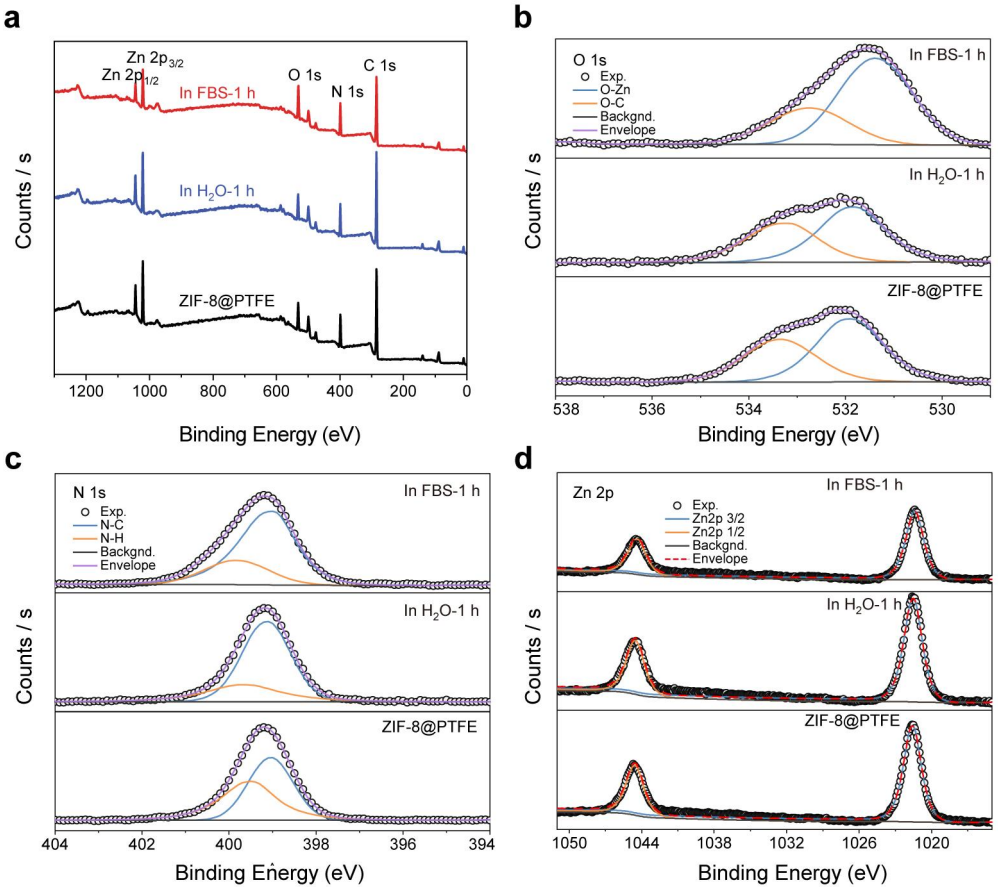

Figure S7. XPS characterizations of ZIF-8@PTFE after immersion in deionized water or FBS. (a) XPS survey spectra. High-resolution XPS spectra of (b) O 1s spectra, (c) N 1s spectra, (d) Zn 2p spectra.

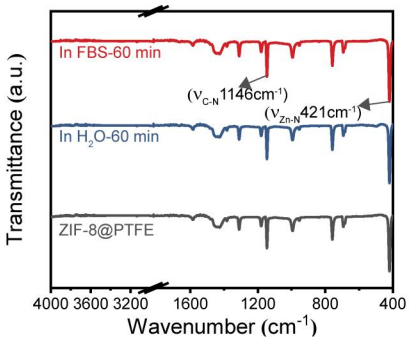

Figure S8. ATR-FTIR analysis of ZIF-8@PTFE after immersed in water and FBS for 60 min.

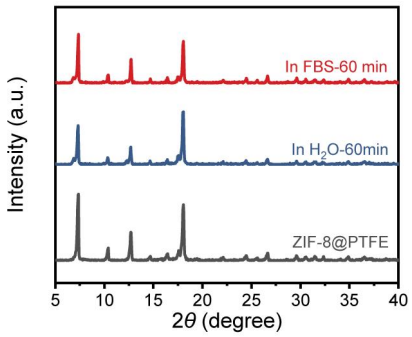

Figure S9. PXRD patterns of ZIF-8@PTFE after immersed in water and FBS.

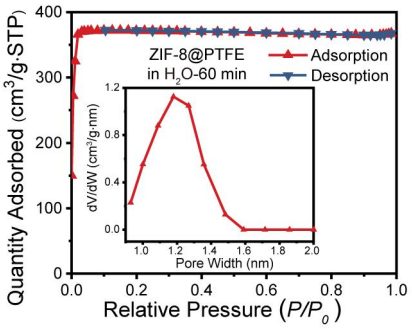

Figure S10. Nitrogen adsorption-desorption isotherms of ZIF-8@PTFE after immersed in water for 60 min. After immersed in water, the BET surface area is 1541 m^2/g and micropore volume is 0.57 cm^3/g.

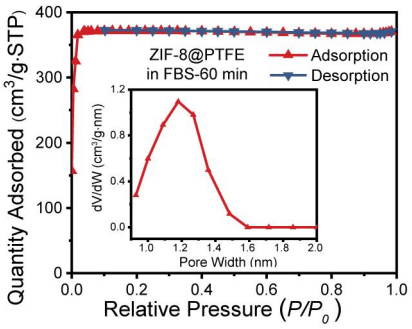

Figure S11. Nitrogen adsorption-desorption isotherms of ZIF-8@PTFE after immersed in FBS for 60 min. After immersed in FBS, the BET surface area 1515 m^2/g and micropore volume is 0.57 cm^3/g.

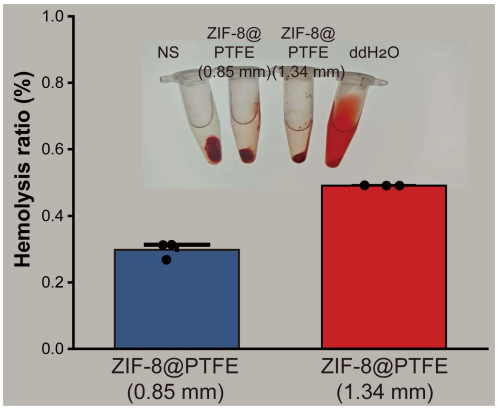

Figure S12. The hemolysis experiment of the thin ZIF-8@PTFE (0.85 mm) and the thick ZIF-8@PTFE (1.34 mm). The hemolysis ratios were 0.3 % and 0.5 % for the thin and thick samples, respectively (n = 3 independent replicates).

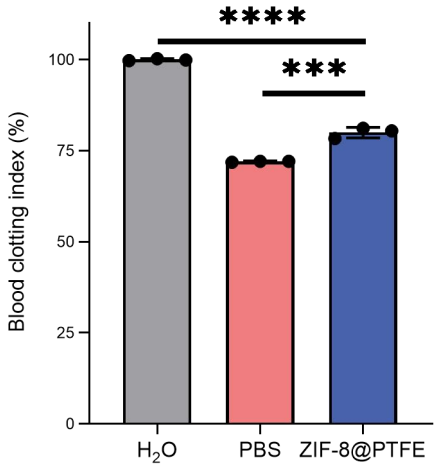

Figure S13. Blood clotting index of the ZIF-8@PTFE. Statistical analysis was performed using two-tailed Student's t-test. ***$p < 0.001$, ****$p < 0.0001$, $n = 3$ independent replicates.

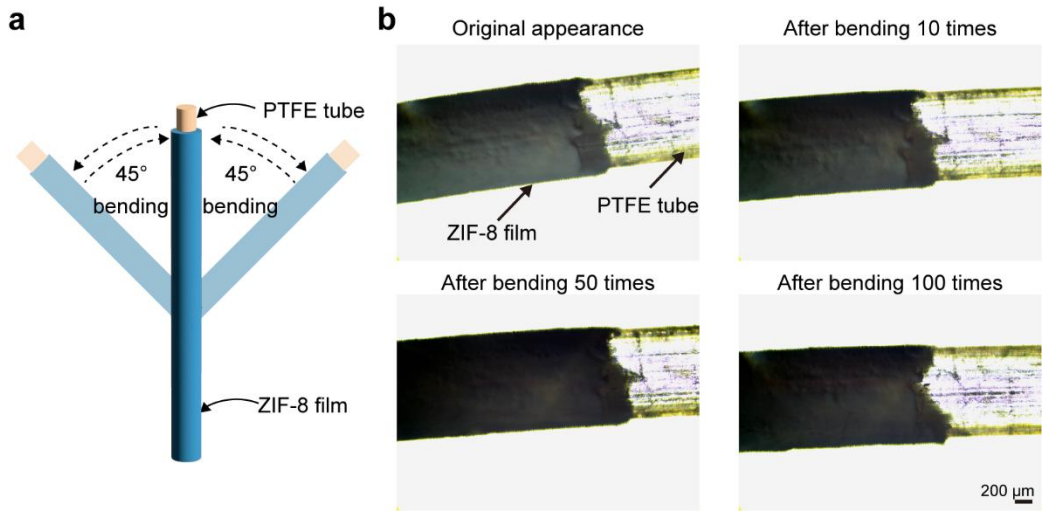

Figure S14. (a) Schematic illustration of the bending test, and (b) Optical microscope images of the ZIF-8@PTFE after multiple bending cycles (bending angle is 45°).

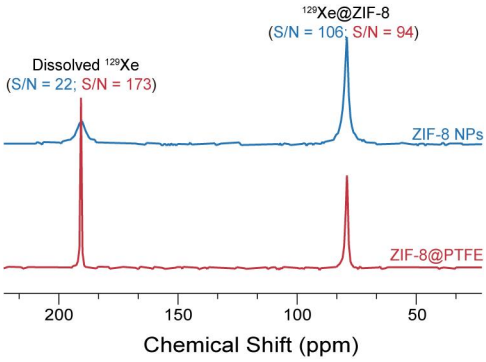

Figure S15. Hyperpolarized ^{129}Xe NMR spectra of pristine ZIF-8 nanoparticles (11.6 mg/mL) and the ZIF-8@PTFE (the concentration of loaded ZIF-8 on PTFE is 11.6 mg/mL). Full Widths at Half Maximum (FWHM) of ZIF-8 NPs: 492 Hz for dissolved ^{129}Xe, 214 Hz for ^{129}Xe@ZIF-8; FWHM of ZIF-8@PTFE: 48 Hz for dissolved ^{129}Xe, 128 Hz for ^{129}Xe@ZIF-8. LB = 30 Hz, NS= 1.

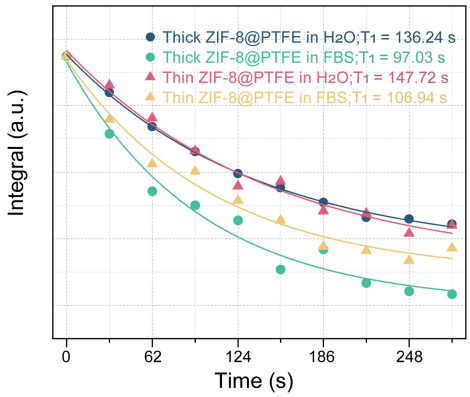

Figure S16. The collected apparent T_1 relaxation time of entrapped ^{129}Xe for thick ZIF-8@PTFE (outer diameter 1.34 mm, inner diameter 1.0 mm) and thin ZIF-8@PTFE (outer diameter 0.85 mm, inner diameter 0.5 mm) in deionized water or in FBS.

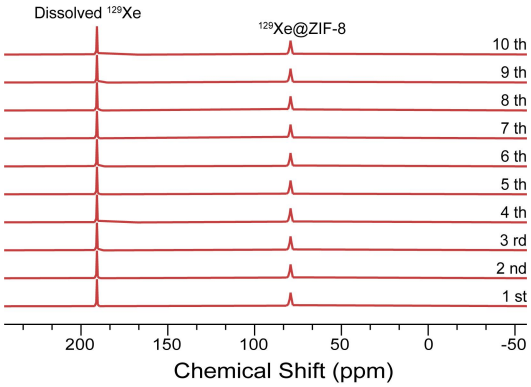

Figure S17. The corresponding ^{129}Xe NMR spectra for 7 segments of ZIF-8@PTFE under 10 consecutive samplings.

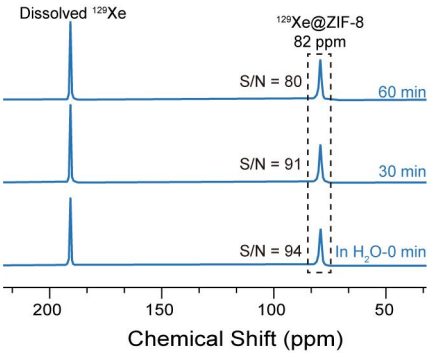

Figure S18. Hyperpolarized ^{129}Xe NMR spectra of ZIF-8@PTFE after immersed in water. NS = 1, LB = 30 Hz.

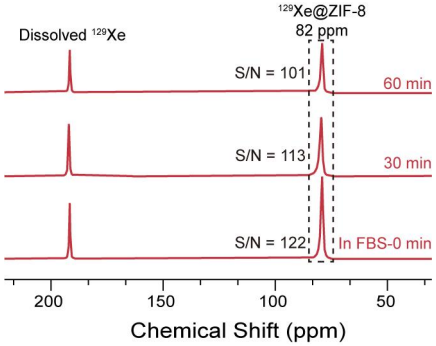

Figure S19. Hyperpolarized ^{129}Xe NMR spectra of ZIF-8@PTFE after immersed in FBS. NS = 1, LB = 30 Hz.

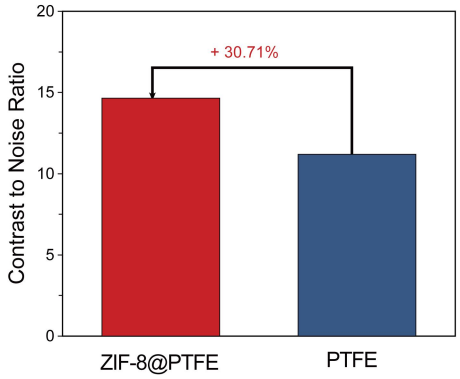

Figure S20. Comparison of the contrast to noise ratio (CNR) between ZIF-8@PTFE and PTFE tube without ZIF-8 flim on ^{1}H MR axial images. CNR of ZIF-8@PTFE = 14.64; CNR of PTFE = 11.2.

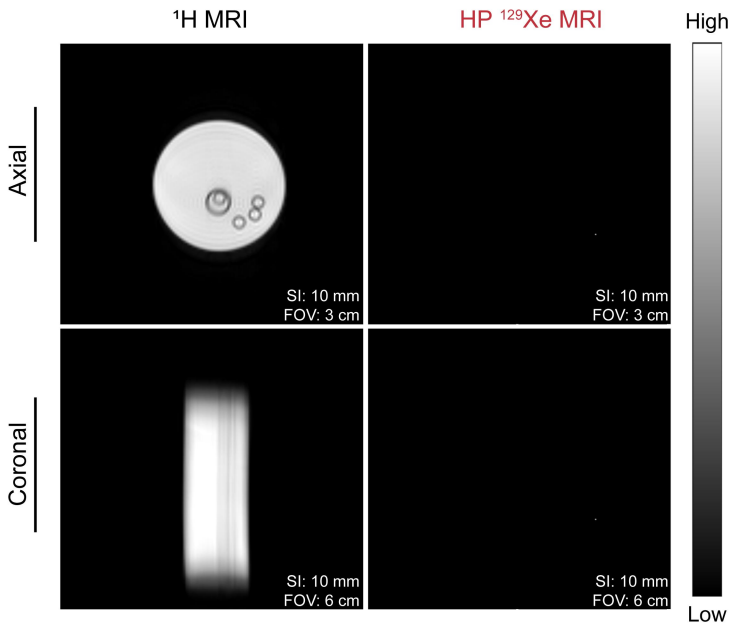

Figure S21. MR images of the PTFE tube without ZIF-8 film decoration.

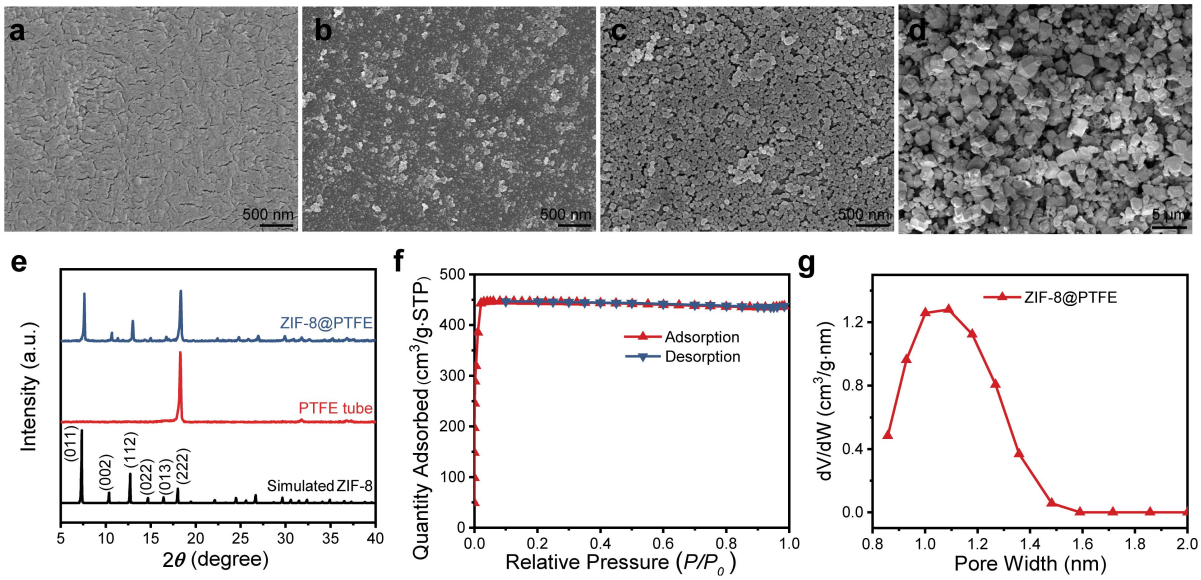

Figure 22. The morphology and properties of thin ZIF-8@PTFE (0.85 mm). Top-view SEM images of (a) pristine thin PTFE tube, (b) Zn-PDA layer coated thin PTFE, (c) activated Zn-PDA layer coated thin PTFE, (d) thin ZIF-8@PTFE. (e) XRD patterns of pristine thin PTFE tube and thin ZIF-8@PTFE. (f) Nitrogen adsorption-desorption isotherms of thin ZIF-8@PTFE. (g) The corresponding micropore size distribution.

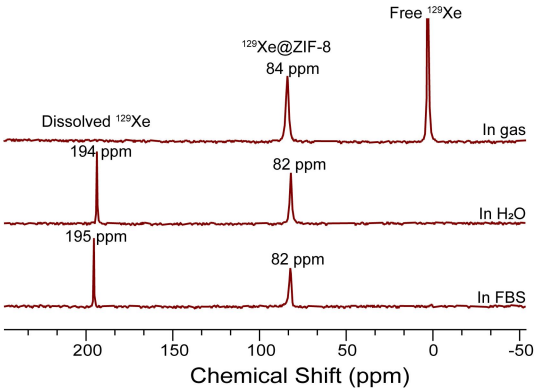

Figure S23. ^{129}Xe NMR spectra of thin ZIF-8@PTFE (0.85 mm) in different environments (NS = 1, LB = 15 Hz).

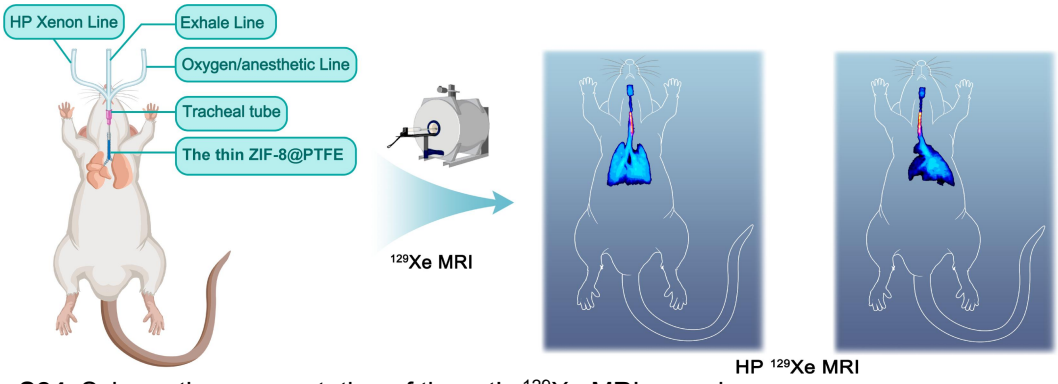

Figure S24. Schematic representation of the rat's ^{129}Xe MRI scanning.

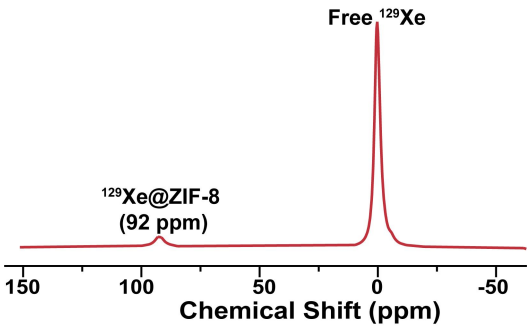

Figure S25. ^{129}Xe NMR spectrum of the ZIF-8@PTFE at the trachea of the rat (NS = 1, LB = 100 Hz).

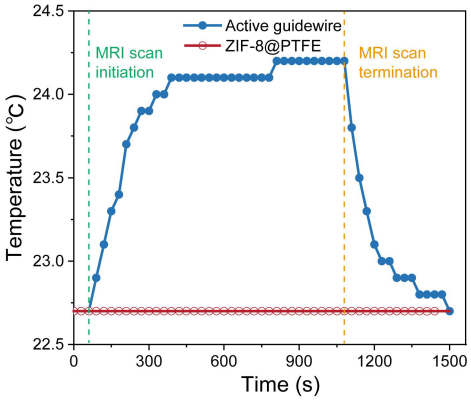

Figure S26. Radiofrequency induced heating of the ZIF-8@PTFE and the active guidewire.

Table S1. ICP-OES of Zn^{2+} in the leaching solution from an 8 cm ZIF-8@PTFE under different immersion durations (10 mL TM buffer, pH = 7.5). Each time point was measured in triplicate (n=3), and mean values are presented. Corresponding ZIF-8 mass loss rates were calculated from its molecular formula $Zn(C_4H_6N_2)_2$.

	$C_{Zn^{2+}}$ (μg mL^{-1})	Mass loss rate of ZIF-8 (%)
0 h	---	---
0.5 h	5.79±0.04	2.89±0.02
1.0 h	12.55±0.11	6.23±0.06

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