Supporting Information

Covalent Organic Framework-Based Spherical Nucleic Acid Probe with a Bonding-Defect Amplified Modification Strategy

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1. Experimental Section

Materials and reagents.

5,10,15,20-tetrakis(4-aminophenyl)-21H,23H-porphine (Tph) and 2,5-dihydroxyterephthalaldehyde (Dha) were obtained from Changchun Third Party Pharmaceutical Technology Co. Ltd. DNA oligonucleotides were synthesized and purified by Sangon Biotechnology Co., Ltd (Shanghai, China) and the sequences of these oligonucleotides are shown in Table S1. Deoxyribonuclease I (DNase I) was purchased from Solarbio Science and Technology (Beijing, China). 3-(4,5-dimethylthiazol-2-yl)-2,5- diphenyltetrazolium bromide (MTT) was purchased from Sigma Chemical Company. Confocal dish was purchased from Cellvis, Mountain View, CA. The human breast cancer cell line (MCF-7), normal immortalized human mammary epithelial cell line (MCF-10A) were purchased from Procell (Wuhan, China). All the other chemical reagents were of analytical grade and used without further purification.

Instruments.

Fourier infrared spectrometer (Nicolet iS50 FT-IR) was used to characterize the infrared spectrum. Powder X-ray diffraction (XRD) pattern was obtained on a Rigaku SmartLab SE X-Ray Powder Diffractometer with Cu Kα line focused radiation (λ = 1.5405 Å). Transmission electron microscopy (TEM, HT7700, Japan) was carried out to characterize the morphology of the nanoparticles. Scanning electron microscopy (SEM) micrographs were recorded on a Hitachi SU8010 Scanning Electron Microscope. UV-vis spectroscopy was achieved with UV-1700 (Shimadzu, Japan). Fluorescence spectra were obtained using a FLS-980 Edinburgh Fluorescence Spectrometer with a Xenon lamp. The absorbance was measured in a microplate reader (Synergy 2, Biotek, USA) for the MTT assay. Confocal fluorescence imaging studies were performed using a TCS SP8 confocal laser scanning microscope (Leica, Germany). All pH measurements were performed with a digital pH-meter (pH-3e, LeiCi, China). Imaging flow cytometry was accomplished on Amnis ImageStream MarkII (Merck Millipore, Seattle, WA).

Preparation of COF NPs. COF NPs were prepared according our previous method without alternation.[1]

2. Supplementary Figures and Table

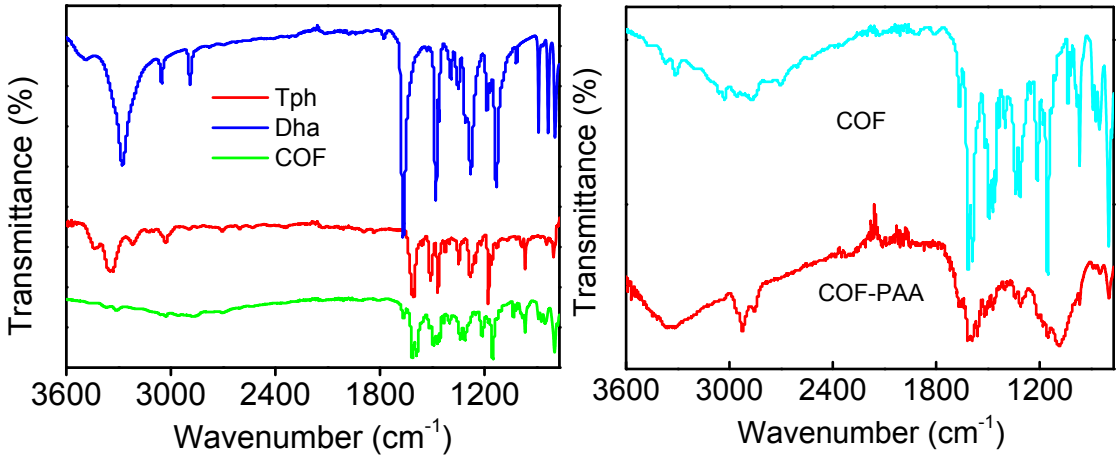

Figure S1. FTIR spectra of Tph, Dha, COF and COF-PAA.

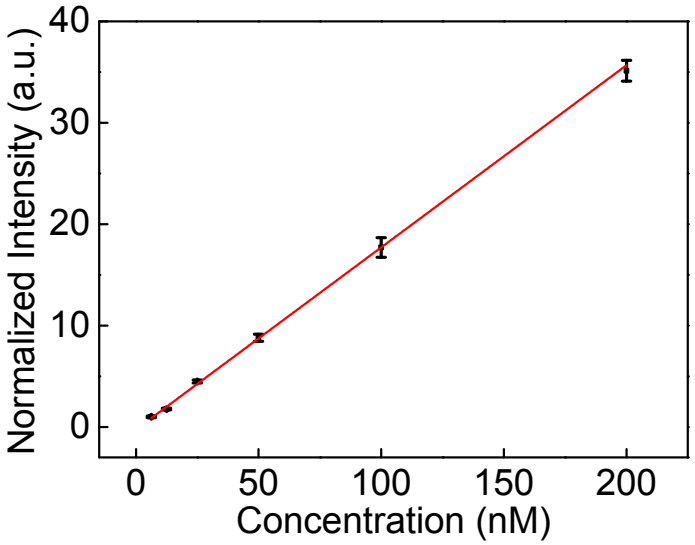

Figure S2. The fluorescence standard curve of c-myc.

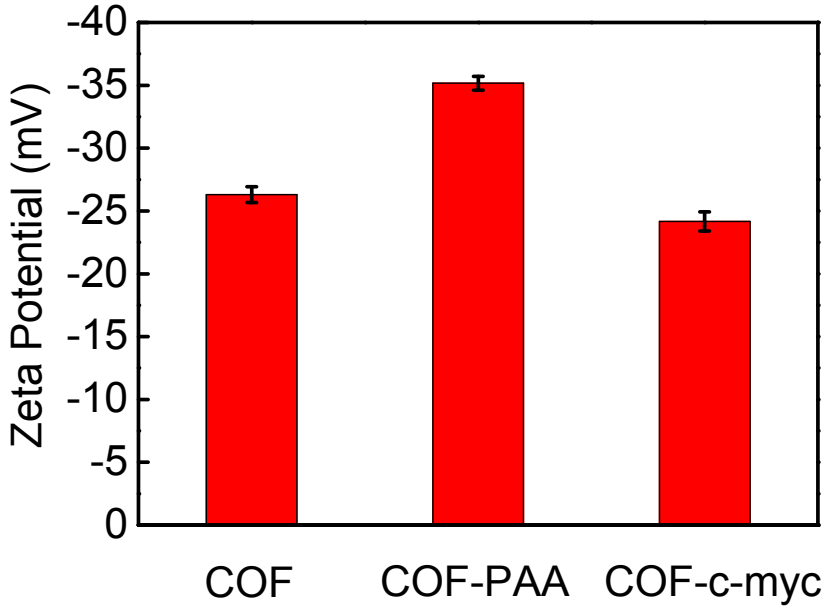

Figure S3. The Zeta potential of COF, COF-PAA, COF-c-myc.

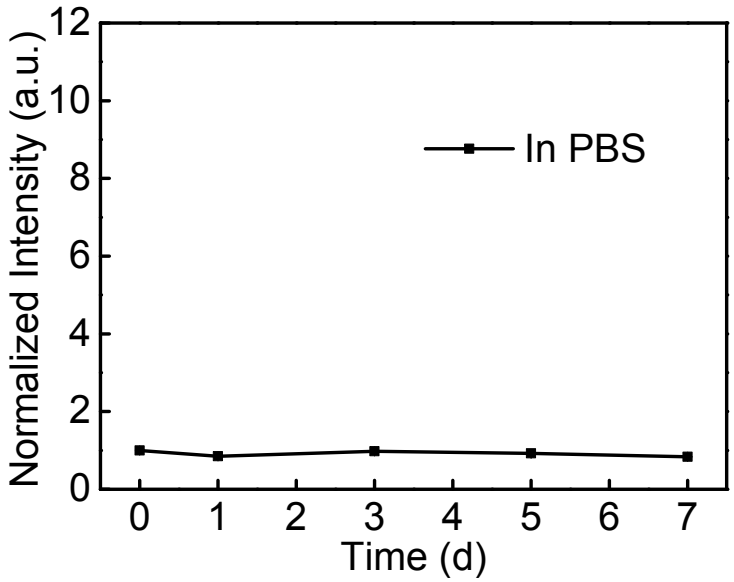

Figure S4. The storage stability of COF-c-myc in PBS solution.

Table S1. DNA sequences employed in this work

Oligonucleotide	**Sequence (5′-3′)**
c-myc	Cy3-CAGTTGGTGAAGCTAACGTTGAGCAACTGAAAAAA-NH_2
T-c-myc:	CTCAACGTTACGTTCAC
T-c-myc-mt:	CTCAACGTT***G***CGTTCAC
T-221:	AGCTACATTGTCTGCTGGGTTTC
T-21:	TAGCTTATCAGACTGATGTTGA
T-TK1:	AAGTATGCCAAAGACACTCGC

References

1. Gao, P.; Wang, M.; Chen, Y.; Pan, W.; Zhou, P.; Wan, X.; Li, N.; Tang, B., A COF-based nanoplatform for highly efficient cancer diagnosis, photodynamic therapy and prognosis. *Chem. Sci.* **2020,** *11* (26), 6882-6888.