

Supporting Information

Single wavelength excited multi-channel nanoMOFs
sensor for simultaneous and ratiometric imaging of
intracellular pH and O₂

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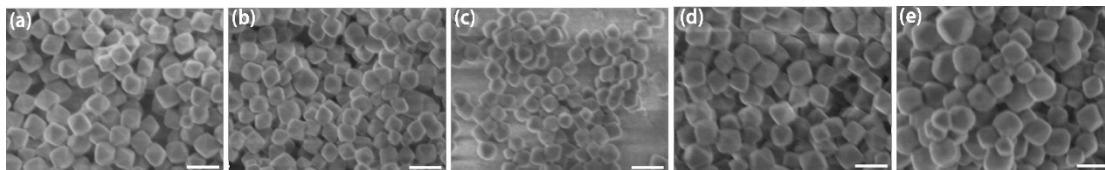


Fig. S1 SEM images of FITC@UiO-66 with different feed ratios of FITC to BDC. The feed ratios were set as (a) 0.006 : 1, (b) 0.012 : 1, (c) 0.024 : 1, (d) 0.048 : 1 and (e) 0.096 : 1 (scale bar: 200 nm).

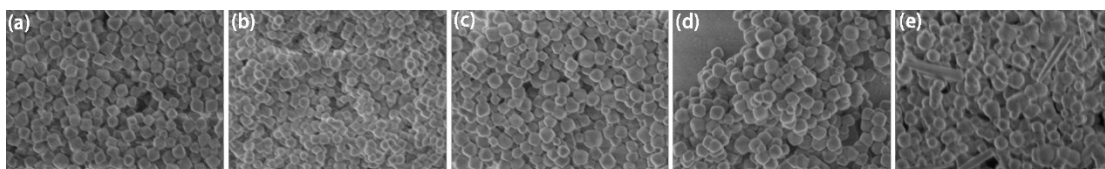


Fig. S2 SEM images of Pt-TCPP@UiO-66 with different feed ratios of Pt-TCPP to BDC. The feed ratios were set as (a) 0.01 : 1, (b) 0.03 : 1, (c) 0.06 : 1, (d) 0.10 : 1 and (e) 0.12 : 1 (scale bar: 200 nm).

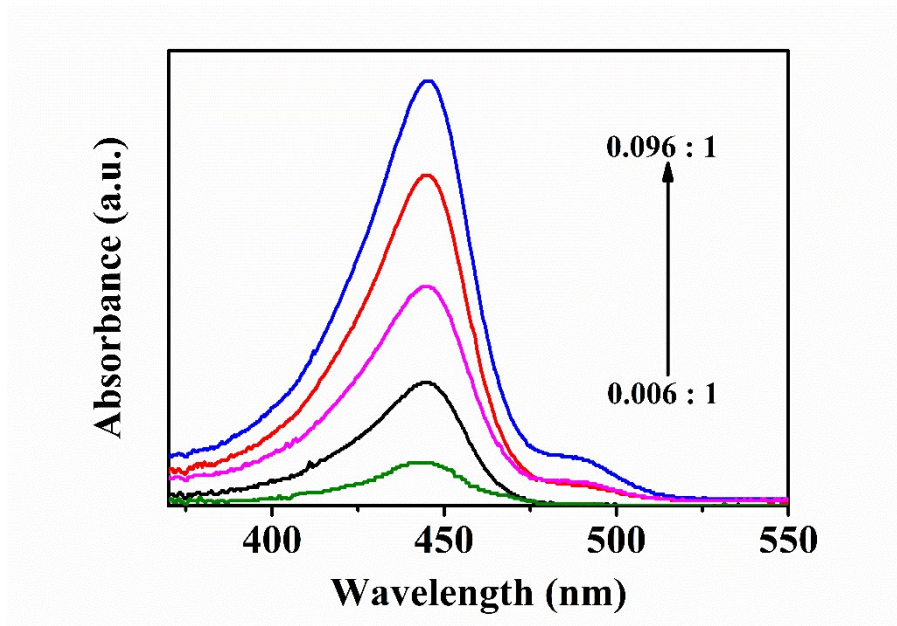


Fig. S3 UV-vis absorption spectra of the FITC@UiO-66 with the FITC to BDC feed ratios ranging from 0.006 : 1 to 0.096 : 1.

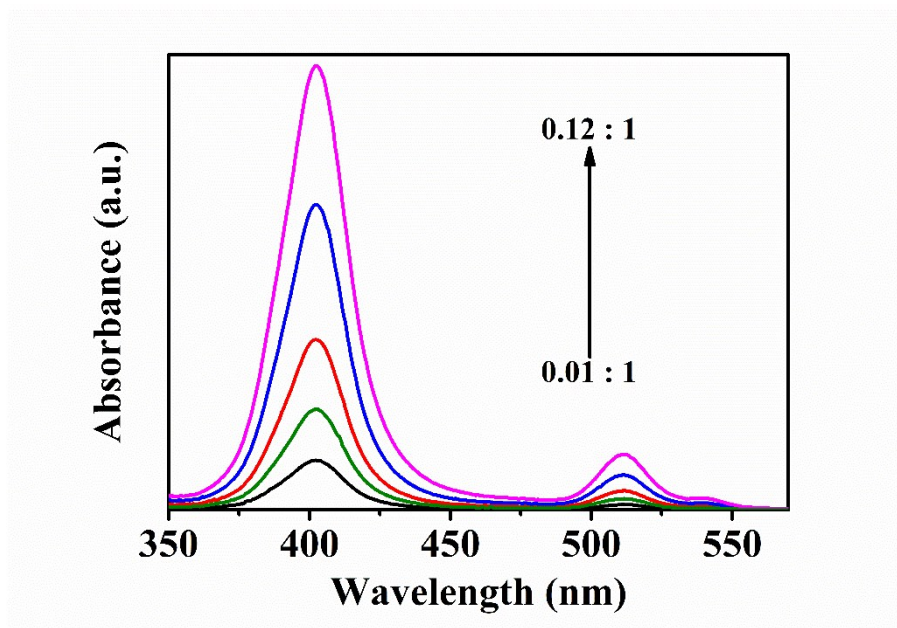


Fig. S4 UV-vis absorption spectra of the Pt-TCPP@UiO-66 with the Pt-TCPP to BDC feed ratios ranging from 0.01 : 1 to 0.12 : 1.

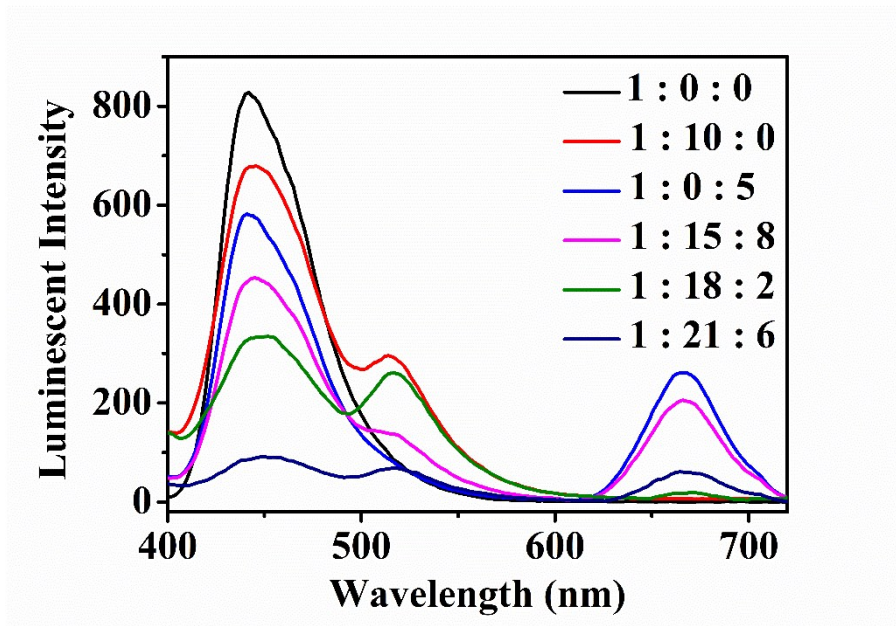


Fig. S5 The emission spectra of the TBAPY/FITC/Pt-TCPP@UiO-66 with various feed ratios of TBAPY : FITC : Pt-TCPP. The excitation wavelength is 385 nm.

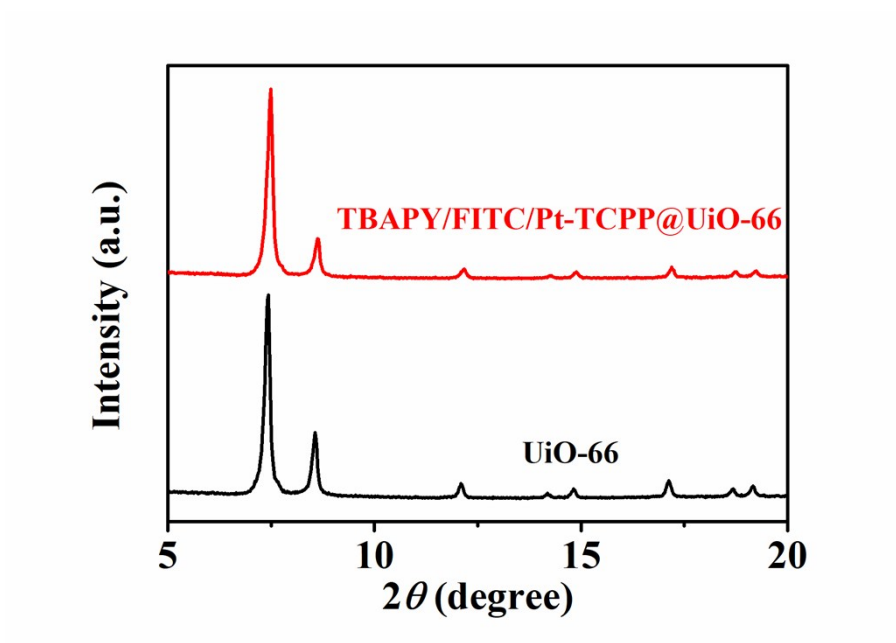


Fig. S6 XRD patterns of the synthesized UiO-66 and TBAPY/FITC/Pt-TCPP@UiO-66.

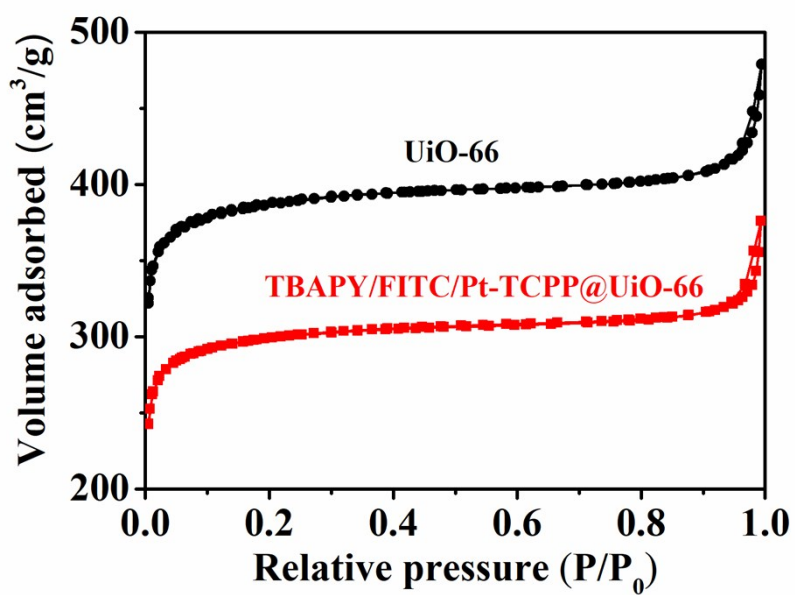


Fig. S7 N₂ sorption isotherms of the synthesized UiO-66 and TBAPY/FITC/Pt-TCPP@UiO-66 samples.

Table S1 Textural parameters of the synthesized UiO-66 and TBAPY/FITC/Pt-TCPP@UiO-66.

Samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V ($\text{cm}^3 \text{g}^{-1}$)
Pure UiO-66	1494	0.52
TBAPY/FITC/Pt-TCPP@UiO-66	1156	0.39

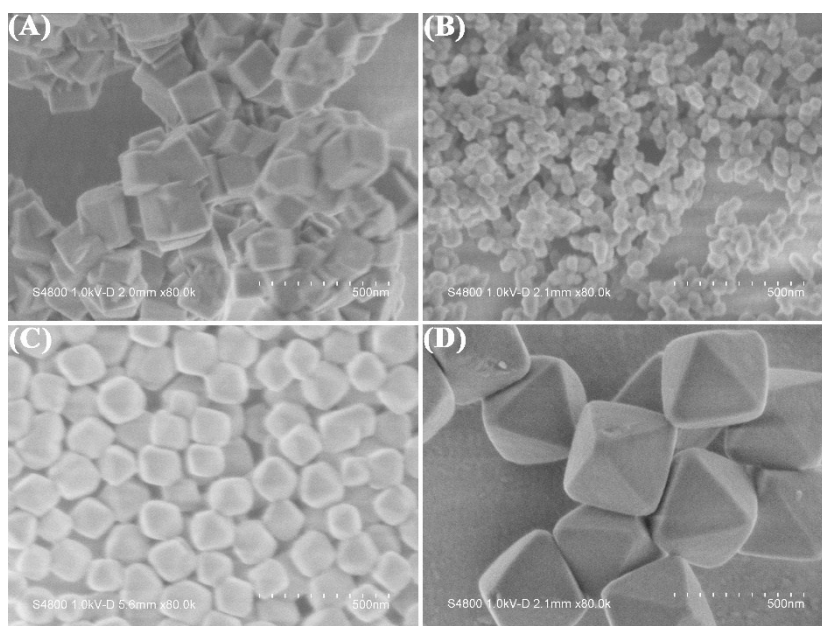


Fig. S8 SEM images of the TBAPY/FITC/Pt-TCPP@UiO-66 NPs synthesized with BA to BDC feed ratios of (A) 0 : 1, (B) 5 : 1, (C) 10 : 1 and (D) 20 : 1 to demonstrate the morphology evolution.

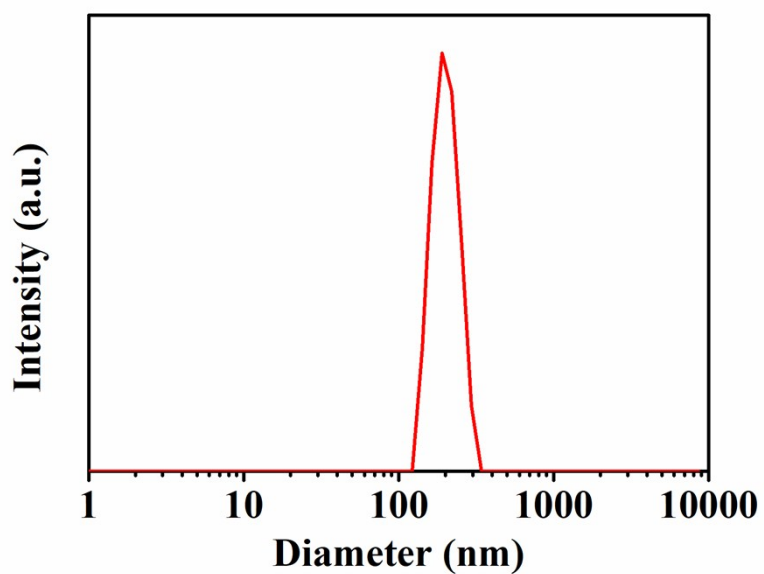


Fig. S9 The DLS profile of the synthesized TBAPY/FITC/Pt-TCPP@UiO-66 dispersed in aqueous phase.

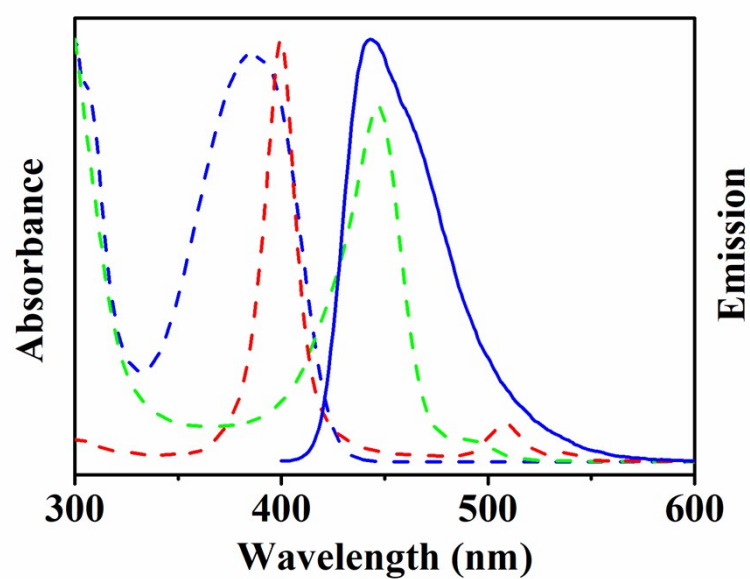


Fig. S10 UV-Vis absorption spectra of Pt-TCPP (dashed red line), FITC (dashed green line) and TBAPY (dashed blue line); and emission spectrum of the TBAPY (solid blue line).

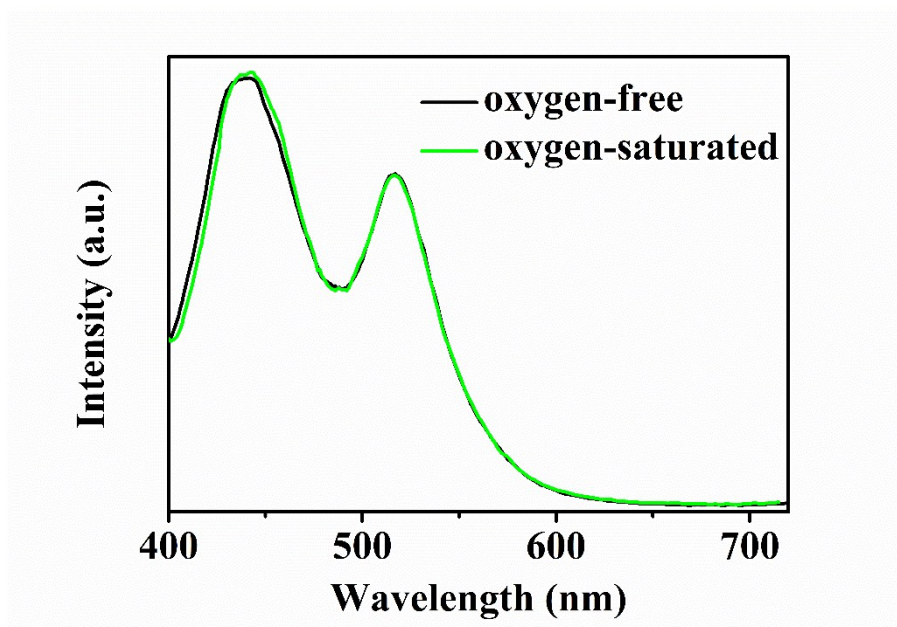


Fig. S11 The emission spectra of the synthesized TBAPY/FITC@UiO-66 under different oxygen concentrations.

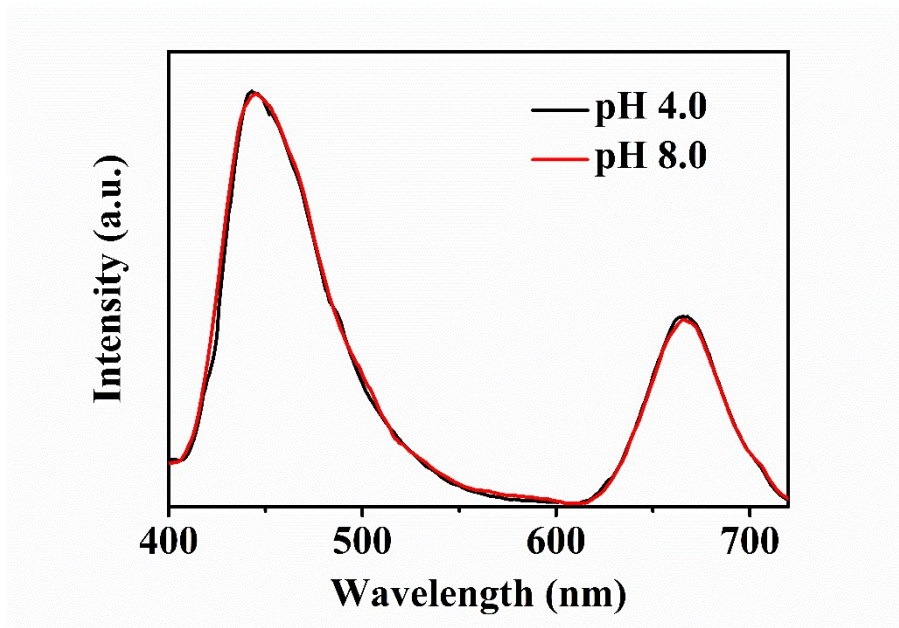


Fig. S12 The emission spectra of the synthesized TBAPY/Pt-TCPP@UiO-66 under different pH conditions.

The limit of detection (LOD) of nanoprobe for pH detection was calculated by the formula of $LOD = 3 \sigma / k$.

$$\begin{aligned}
 \text{Detection Limit} &= 3\sigma/k \\
 &= 3 \times 1.22 / 79.8 \\
 &= 0.0459
 \end{aligned}$$

The luminescence spectra of TBAPY/FITC/Pt-TCPP@UiO-66 probe at pH = 7 were recorded for 6 times. The standard deviation σ of the sample was calculated to be 1.22.

The slope k is obtained by fitting a linear relationship between the luminescent intensity of the sample at 515 nm and pH.

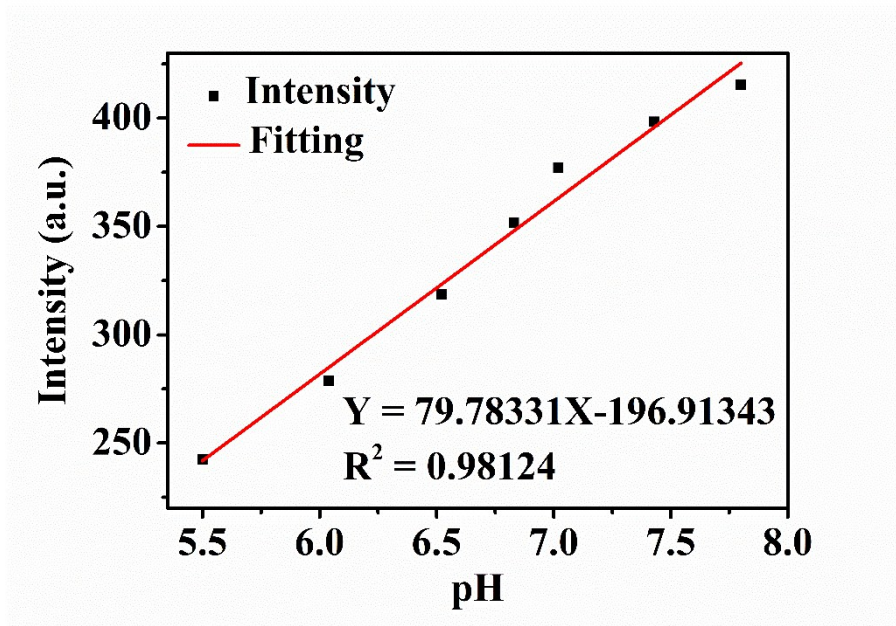


Fig. S13 The relationship between the luminescent intensity of TBAPY/FITC/Pt-TCPP@UiO-66 probe at 515 nm and pH, and its linear fitting curve are used to estimate the LOD at a DO concentration of 7 mg/L.

Table S2 Comparison of the sensing performances between TBAPY/FITC/Pt-TCPP@UiO-66 and the reported pH sensors.

Matrix	Formation	Response range	LOD	Ref.
	TBAPY/FITC/Pt-TCPP@UiO-66	pH 4.51-8.21	0.0459	This work
MOFs	FITC@F-UiO NMOFs	pH 4-8	/	[1]
	Tb-MOF	pH 2-7	/	[2]
	UiO-66-N=N-ind _{3h}	pH 1-12	/	[3]
	UPC-5	pH 7.5-10.0	/	[4]
Others	FITC@Semiconducting Polymer Dots	pH 5-8	/	[5]
	FITC@Polymer Sensor Film	pH 3-8	/	[6]
	FITC@SiO ₂ @QD	pH 5.56-7.86	/	[7]
	FITC@Core/shell Nanosensors	pH 3-9	/	[8]
	FITC@Chitosan Film	pH 4-8	/	[9]
	FITC@Semiconducting Polymer Dots	pH 4.08-9.01	/	[10]

The limit of detection (LOD) of nanoprobe for O₂ detection was calculated by the formula of $LOD = 3 \sigma / k$.

$$\begin{aligned} \text{Detection Limit} &= 3\sigma/k \\ &= 3 \times 1.24 / 28.3 \\ &= 0.1314 \text{ mg/L} \end{aligned}$$

The luminescence spectra of TBAPY/FITC/Pt-TCPP@UiO-66 probe at DO = 7 mg/L were recorded for 6 times. The standard deviation σ of the sample was calculated to be 1.24. The slope k is obtained by fitting a linear relationship between the luminescent intensity of the sample at 668 nm and DO.

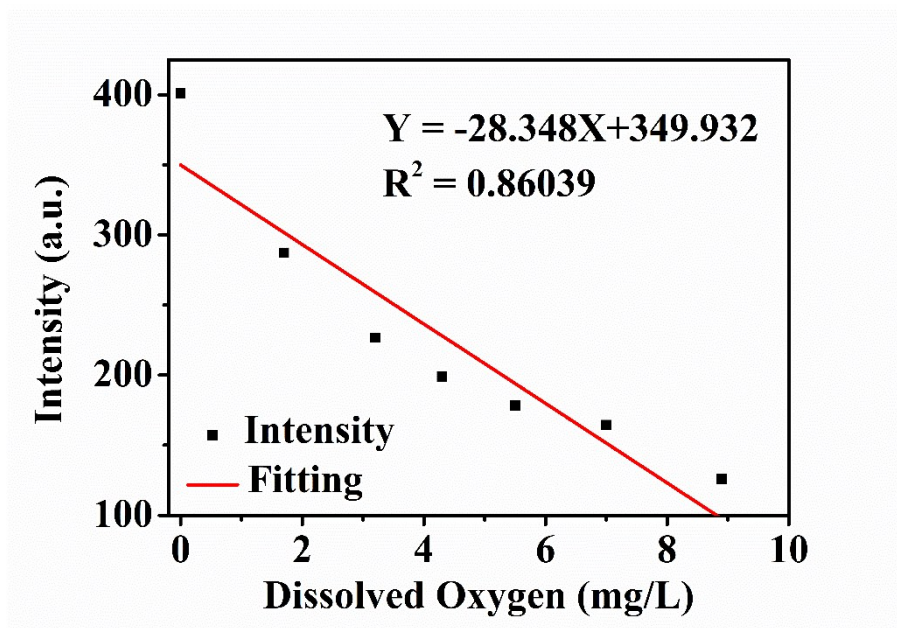


Fig. S14 The relationship between the luminescent intensity of TBAPY/FITC/Pt-TCPP@UiO-66 probe at 668 nm and DO, and its linear fitting curve are used to estimate the LOD in aqueous phase at pH = 6.9.

Table. S3 Comparison of the sensing performances between TBAPY/FITC/Pt-TCPP@UiO-66 and the reported O₂ sensors.

Matrix	Formation	Response range	LOD	Ref.
	TBAPY/FITC/Pt-TCPP@UiO-66	0-30 mg/L	0.1314 mg/L	This work
MOFs	R-UiO NMOFs	0-80 mmHg	/	[11]
	PCN-224(Pt)	0-731 μ M	/	[12]
	UiO-67	0.001-0.026 atm	/	[13]
	MIL-100(In) \Rightarrow Tb ³⁺ Film	0 -1 atm	/	[14]
	Pt-TCPP@Films onto Alumina Plates	0-100%	/	[15]
	Pt-TPP Polymer	4.3-38.6 mg/L	0.06 mg/L	[16]
Others	Pt-TCPP@Fluoropolymer Film	0-100%	/	[17]
	Pt-FTPP	0-15.5 mg/L	0.01 mg/L	[18]
	PtOEP Film	0-40 mg/L	/	[19]

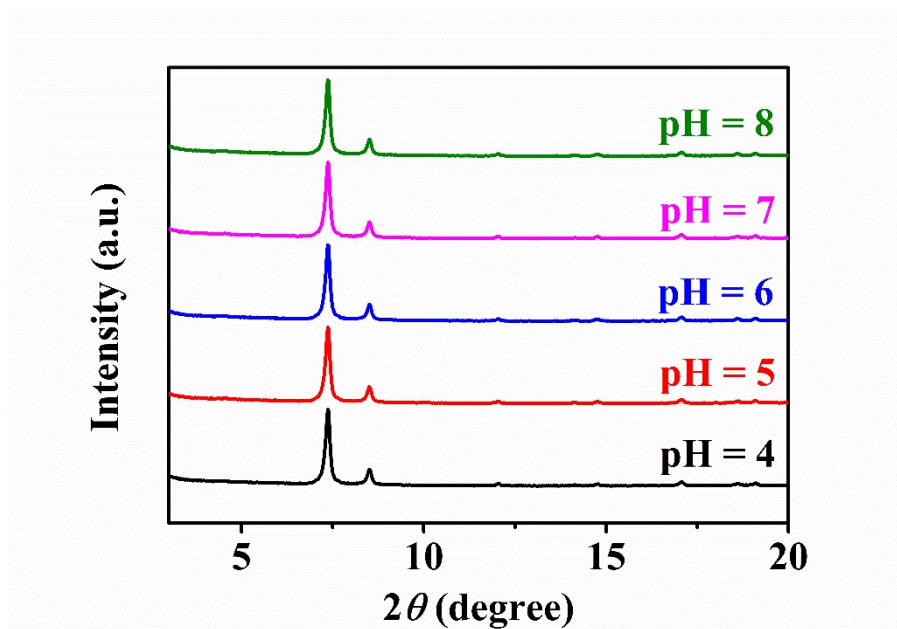


Fig. S15 XRD patterns of the TBAPY/FITC/Pt-TCPP@UiO-66 after soaking and keeping in a buffer solution of different pH for 24 h.

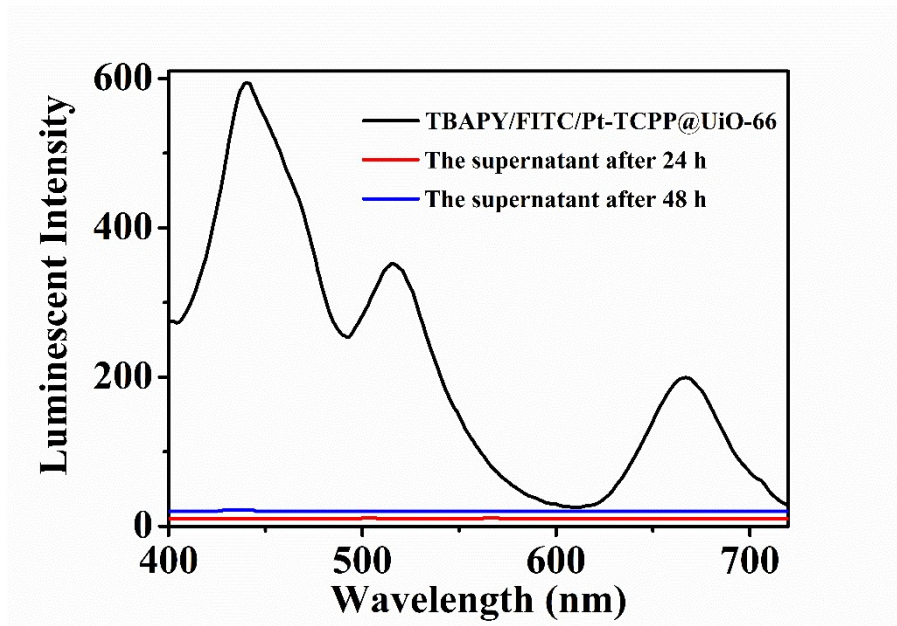


Fig. S16 Luminescent spectra of the synthesized nanoprobe and the supernatant isolated from the nanoprobe aqueous suspension after 24 and 48 h.

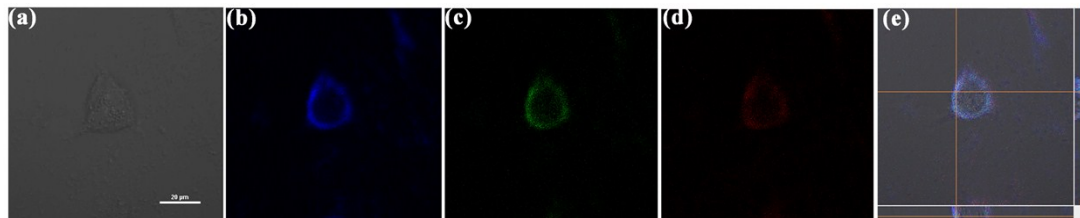


Fig. S17. Luminescent images of HeLa cells treated with the TBAPY/FITC/Pt-TCPP@UiO-66 (pH = 7.4, DO = 8mg/L): (a) bright field image, (b) blue channel image, (c) green channel image, (d) red channel image, (e) orthogonal projection of the z-stack reconstructions of consecutive focal planes image.

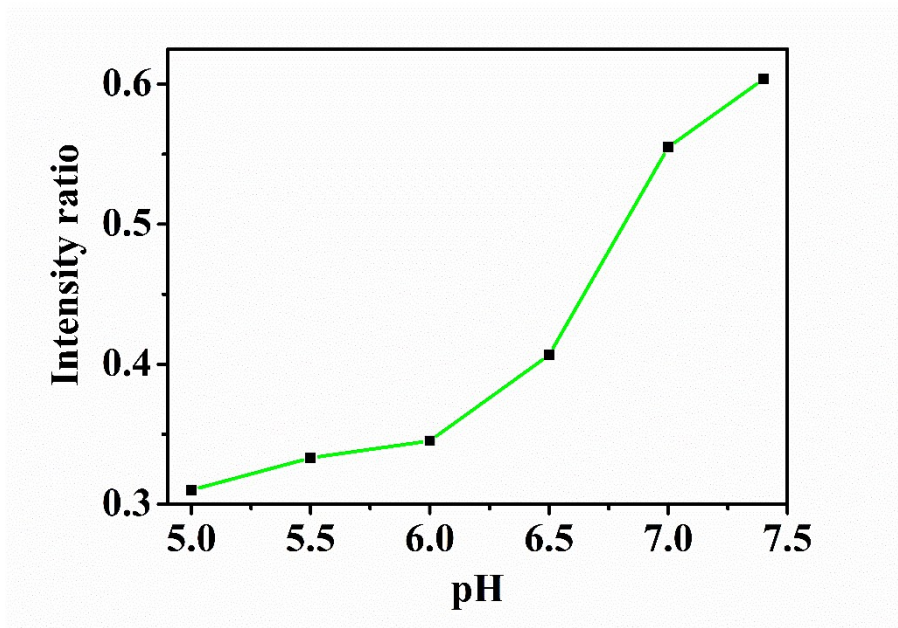


Fig. S18 Calibration curve of the intensity ratio of green/blue channels for TBAPY/FITC/Pt-TCPP@UiO-66 sensor in the pseudo color images under different pH values.

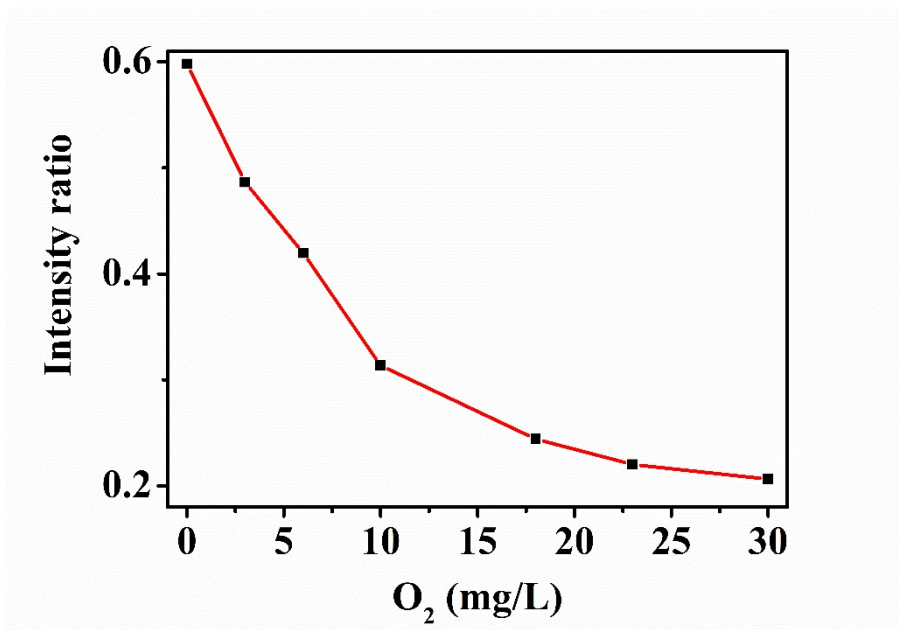


Fig. S19 Calibration curve of the intensity ratio of red/blue channels for TBAPY/FITC/Pt-TCPP@UiO-66 sensor in the pseudo color images under different concentrations of oxygen.

Notes and references

- 1 C. He, K. Lu and W. Lin, *J. Am. Chem. Soc.*, 2014, **136**, 12253.
- 2 H.-Y. Li, Y.-L. Wei, X.-Y. Dong, S.-Q. Zang and T. C. W. Mak, *Chem. Mater.*, 2015, **27**, 1327.
- 3 J. Aguilera-Sigalat and D. Bradshaw, *Chem. Commun.*, 2014, **50**, 4711.
- 4 Qingguo Meng, Xuelian Xin, Liangliang Zhang, Fangna Dai, Rongming Wang and Daofeng Sun, *J. Name.*, 2013, **00**, 1.
- 5 Y.-H. Chan, C. Wu, F. Ye, Y. Jin, P. B. Smith and D. T. Chiu, *Anal. Chem.*, 2011, **83**, 1448.
- 6 R. J. Meier, S. Schreml, X.-D. Wang, M. Landthaler, P. Babilas, and O. S. Wolfbeis, *Angew. Chem.*, 2011, **123**, 11085.
- 7 H. Huang, F. Dong and Y. Tian, *Anal. Chem.*, 2016, **88**, 12294.
- 8 X.-D. Wang, J. A. Stolwijk, T. Lang, M. Sperber, R. J. Meier, J. Wegener and O. S. Wolfbeis, *J. Am. Chem. Soc.*, 2012, **134**, 17011.
- 9 W. Xu, S. Lu, Y. Chen, T. Zhao, Y. Jiang, Y. Wang, X. Chen, *Sensor. Actuat. B-Chem.*, 2015, **220**, 326.
- 10 W. Xu, S. Lu, M. Xu, Y. Jiang, Y. Wang and X. Chen, *J. Mater. Chem. B*, 2016, **4**, 292.
- 11 R. Xu, Y. Wang, X. Duan, K. Lu, D. Micheroni, A. Hu and W. Lin, *J. Am. Chem. Soc.*, 2016, **138**, 2158.
- 12 J. Yang, Z. Wang, Y. Li, Q. Zhuang, and J. Gu, *Chem. Mater.*, 2016, **28**, 2652.
- 13 S. M. Barrett, C. Wang and W. Lin, *J. Mater. Chem.*, 2012, **22**, 10329.
- 14 Z. Dou, J. Yu, Y. Cui, Y. Yang, Z. Wang, D. Yang and G. Qian, *J. Am. Chem. Soc.*, 2014, 136, **15**, 5527.
- 15 Y. Amao and I. Okura, *Analyst*, 2000, **125**, 1601.
- 16 A. S. Holmes-Smith, A. Hamill, M. Campbell and M. Uttamlal, *Analyst*, 1999, **124**, 1463.
- 17 Y. Amao, K. Asai, T. Miyashita and I. Okura, *Polym. Adv. Technol.*, 2000, **11**, 705.
- 18 Y. Zhao, T. Ye, H. Chen, D. Huang, T. Zhou, C. He and X. Chen, *Luminescence*, 2011, **26**, 29.
- 19 R.N. Gillanders, M.C. Tedford, P.J. Crilly, R.T. Bailey, *Analytica Chimica Acta*, 2004, **502**, 1.