Supporting Information

Eu-MOF and its mixed-matrix membranes as fluorescent sensor for quantitative ratiometric pH and folic acid detection, and visible fingerprint identifying

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Experimental section

Material and instruments

All chemical reagents were obtained from commercial sources and used without further purification. Powder X-ray diffraction (XRD) measurements were performed using a SHIMADZU XRD-6000 diffractometer with Cu-Kα radiation (λ = 1.5418 Å). FT-IR spectra were recorded on a Nicolet IS5 spectrometer between 4000 and 400 cm-1 using the KBr pellet method. Elemental analyses (C, H and N) were performed using an Elementar Vario EL cube CHNOS elemental analyzer. Thermogravimetric analyses (TGA) were carried out using a PerkinElmer TGA 7 instrument, with a heating rate of 10 °C min^{-1} under air atmosphere. Photoluminescence analyses were performed on an Edinburgh Instrument FLS 920 luminescence spectrometer. UV-vis absorption measurements were carried out on a Shimadzu UV-3100 spectrophotometer. Scanning electron microscopy (SEM) images and Energy-dispersive X-ray spectroscopy (EDS) were obtained with a JEOL JSM-IT500A instrument. The contact angle was determined with a KRÜSS GmbH DSA-25 instrument.

Determination of crystal structure

A suitable single crystal of 1 was carefully picked out under an optical microscope for single crystal XRD analysis. The intensity data was collected on a Bruker P4 diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation at room temperature. The structure was solved by direct method and refined by full-matrix least-squares on F^2 using OLEX2 equipped with the SHELXTL-2014 crystallographic software packages.[S1-S3] All the hydrogen atoms were placed geometrically and refined in a riding model. All of the non-hydrogen atoms were refined anisotropically. The crystal data and structure refinement for **1** is summarized in Table S1, selected bond lengths and angles are given in Tables S2–S3. CCDC-2081879, contains the supplementary crystallographic data for **1**.
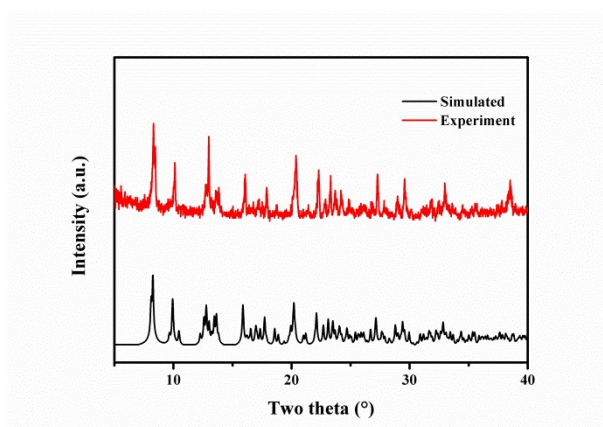
Fig. S1 PXRD patterns of **1**.
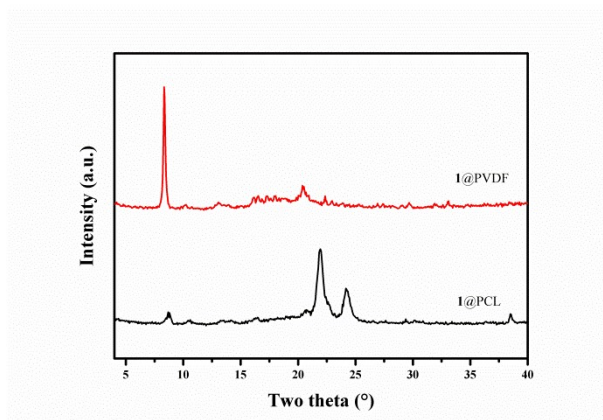
Fig. S2 PXRD patterns of **1**@PCL and **1**@PVDF.
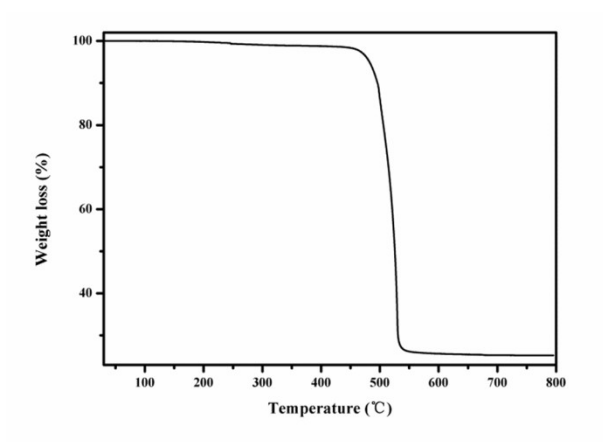
Fig. S3 TGA curve of **1**.
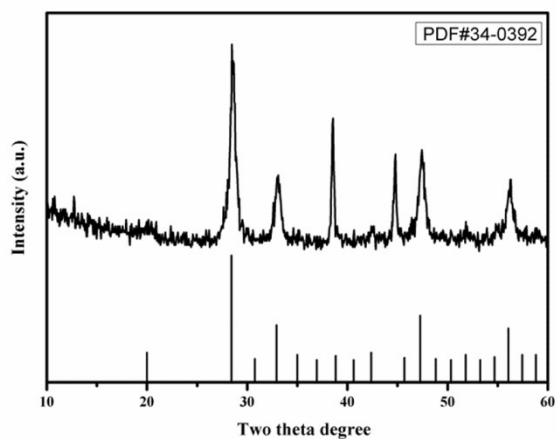
Fig. S4 PXRD patterns of the product after TGA.
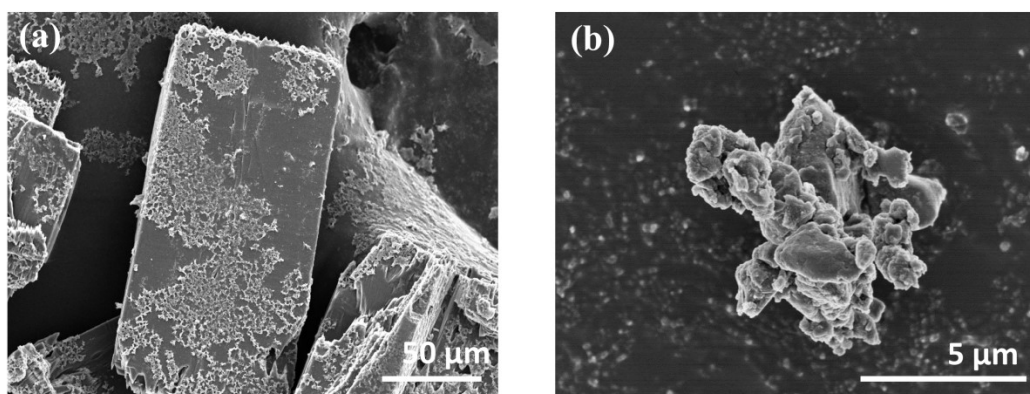
Fig. S5 The SEM images of as-synthesized **1** (a) and grind sample (b).
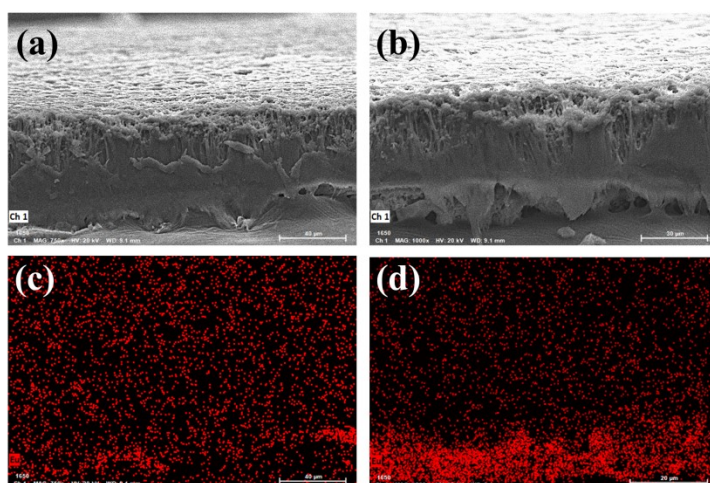
Fig. S6 The cross section SEM images and EDS elemental mapping images (a, c)**1**@PVDF, (b, d)**1**@PCL.
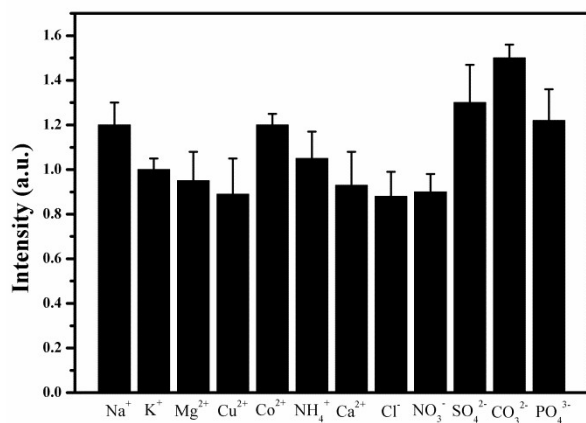
Fig. S7 The effect of ions and anions for FA detection.
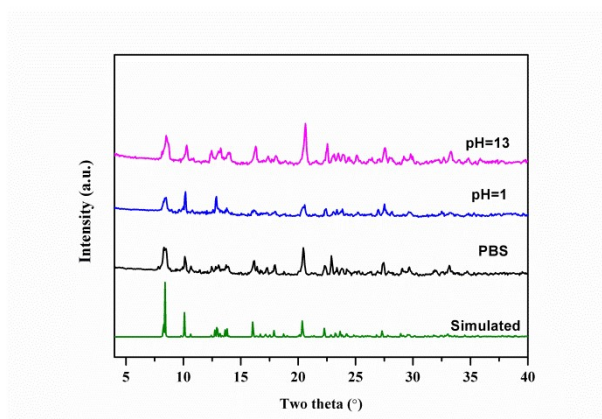
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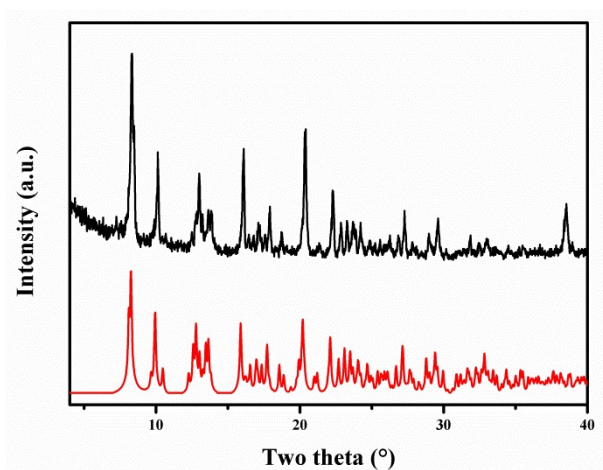
Fig. S9 PXRD pattern of **1** after FA detection.
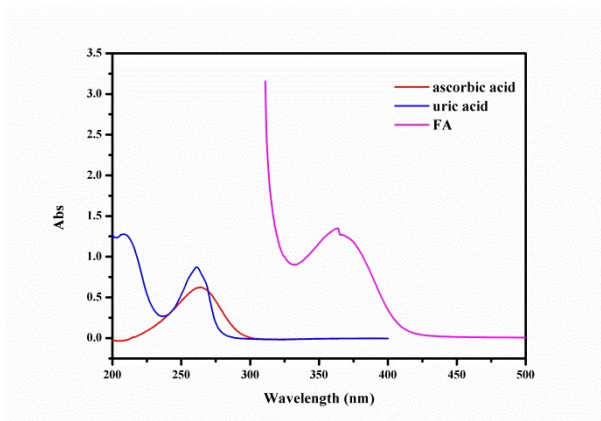
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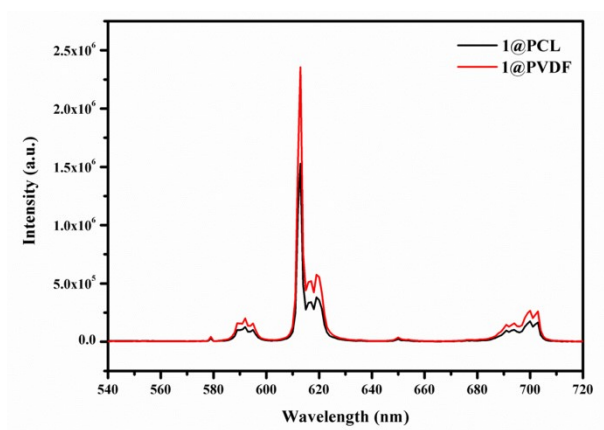
Fig. S11 The fluorescent spectrum of MMMs.
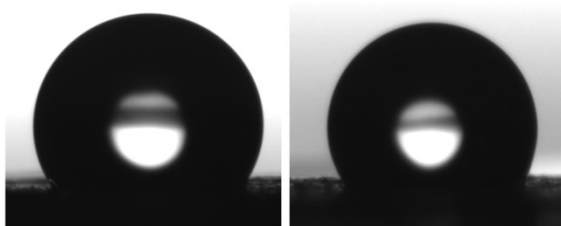
Fig. S12 The contact angle of MMMs. **1**@PCL (left: 118.4°) and **1**@PVDF (right: 119.7°).
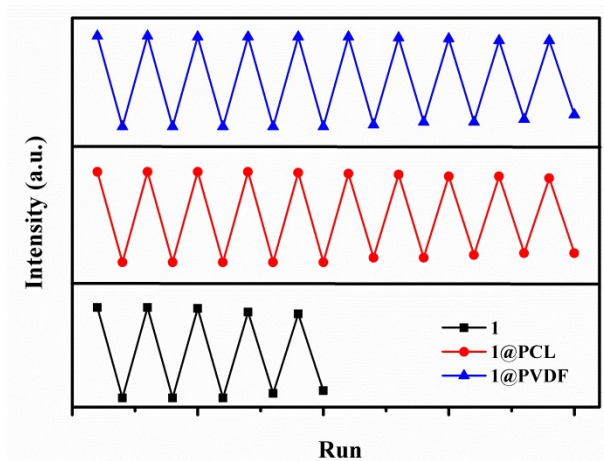
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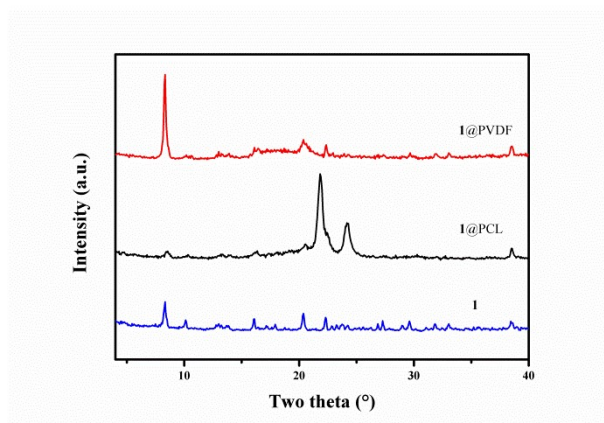
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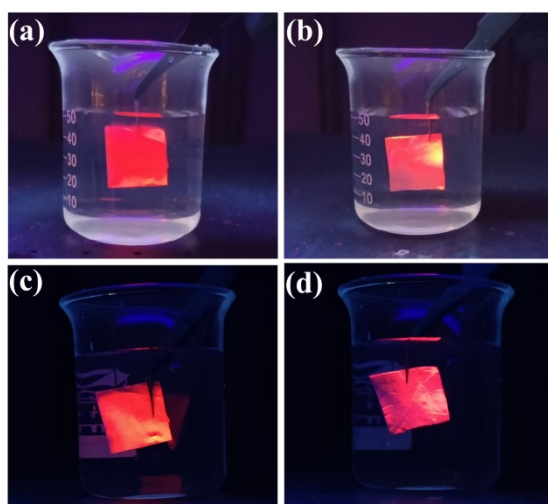
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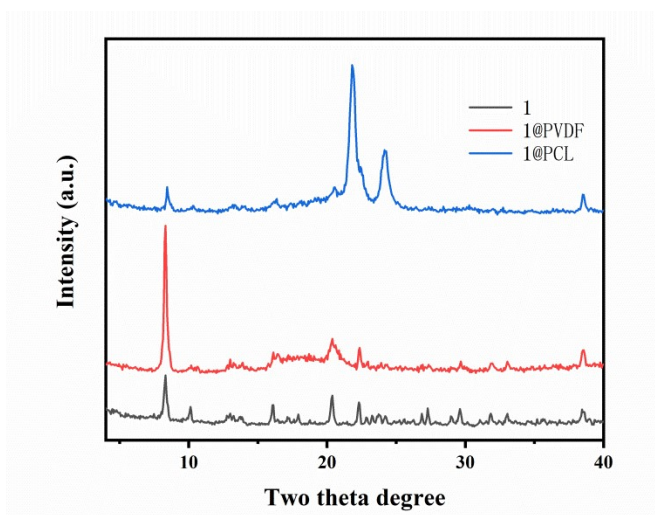
Fig. S16 PXRD patterns of **1**, **1**@PVDF and **1**@PCL after exposed in air for four months.

Table S1 Crystal data and structure refinement for **1**.

Empirical formula	$C_{34}H_{19}EuN_2O_8$
Formula weight	735.47
Temperature/K	293(2) K
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.590(2)
b/Å	16.888(3)
c/Å	14.725(3)
α/°	90.00
β/°	109.92(3)
γ/°	90.00
Volume/Å^3	2709.7(9)
Z	4
ρ_{calc}g/cm^3	1.803
μ/mm^{-1}	2.377
F(000)	1456.0
Crystal size/mm^3	$0.6 \times 0.3 \times 0.3$
Radiation	MoKα ($\lambda = 0.71073$)
2Θ range for data collection/°	6 to 54.86
Index ranges	$-14 \leq h \leq 14, -21 \leq k \leq 21, -16 \leq l \leq 19$
Reflections collected	23474
Independent reflections	6014 [$R_{int} = 0.0623, R_{sigma} = 0.0541$]
Data/restraints/parameters	6014/0/406
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	$R_1 = 0.0351, wR_2 = 0.0630$
Final R indexes [all data]	$R_1 = 0.0504, wR_2 = 0.0689$
Largest diff. peak/hole / e Å^{-3}	0.62/-1.75

Table S2 The selected bond lengths for **1**.

Atom	Atom	Length/Å
Eu1	Eu1[1]	4.2067(7)
Eu1	O1	2.450(3)
Eu1	O2	2.442(3)
Eu1	O8[2]	2.356(3)
Eu1	O4[3]	2.325(3)
Eu1	O7[4]	2.303(3)
Eu1	O3[5]	2.369(3)
Eu1	N1	2.614(4)
Eu1	N2	2.543(3)
Eu1	C8	2.812(4)
Eu1	C22[2]	3.140(4)
O1	C8	1.257(5)
O2	C8	1.271(5)
O8	Eu1[6]	2.356(3)
O8	C22	1.243(5)
O4	Eu1[7]	2.325(3)
O4	C7	1.260(5)
O7	Eu1[8]	2.303(3)
O7	C22	1.263(5)
O3	Eu1[9]	2.369(3)

[1]1-X,1-Y,2-Z; [2]1+X,1/2-Y,1/2+Z; [3]1-X,1/2+Y,3/2-Z; [4]-X,1/2+Y,3/2-Z; [5]+X,1/2-Y,1/2+Z; [6]-1+X,1/2-Y,-1/2+Z; [7]1-X,-1/2+Y,3/2-Z; [8]-X,-1/2+Y,3/2-Z; [9]+X,1/2-Y,-1/2+Z

Table S3 The selected bond angles for **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Eu1	N1	76.76(10)	O7[5]	Eu1	O8[2]	125.84(11)
O1	Eu1	N2	89.96(11)	O7[5]	Eu1	O4[4]	74.27(10)
O1	Eu1	C8	26.50(10)	O7[5]	Eu1	O3[3]	79.98(10)
O1	Eu1	C22[2]	164.21(10)	O7[5]	Eu1	N1	144.01(11)
O2	Eu1	O1	53.32(9)	O7[5]	Eu1	N2	146.89(11)
O2	Eu1	N1	112.59(10)	O7[5]	Eu1	C8	77.88(11)
O2	Eu1	N2	73.46(11)	O7[5]	Eu1	C22[2]	106.31(11)
O2	Eu1	C8	26.84(10)	O3[3]	Eu1	O1	129.73(10)
O2	Eu1	C22[2]	140.34(10)	O3[3]	Eu1	O2	76.70(9)
O8[2]	Eu1	O1	145.82(10)	O3[3]	Eu1	N1	135.46(10)
O8[2]	Eu1	O2	141.96(10)	O3[3]	Eu1	N2	79.71(10)
O8[2]	Eu1	O3[3]	78.00(10)	O3[3]	Eu1	C8	103.31(11)
O8[2]	Eu1	N1	69.07(11)	O3[3]	Eu1	C22[2]	65.32(10)
O8[2]	Eu1	N2	74.43(11)	N1	Eu1	C8	95.50(11)
O8[2]	Eu1	C8	155.50(11)	N1	Eu1	C22[2]	88.51(11)
O8[2]	Eu1	C22[2]	20.43(10)	N2	Eu1	N1	63.40(11)
O4[4]	Eu1	O1	89.74(10)	N2	Eu1	C8	81.70(11)
O4[4]	Eu1	O2	135.10(10)	N2	Eu1	C22[2]	88.43(11)
O4[4]	Eu1	O8[2]	82.90(11)	O4[4]	Eu1	C8	112.60(11)
O4[4]	Eu1	O3[3]	129.36(10)	O4[4]	Eu1	C22[2]	81.10(11)
O4[4]	Eu1	N1	76.00(10)	O7[5]	Eu1	O1	83.25(11)
O4[4]	Eu1	N2	138.29(11)	O7[5]	Eu1	O2	76.58(10)

[1]1-X,1-Y,2-Z; [2]1+X,1/2-Y,1/2+Z; [3]+X,1/2-Y,1/2+Z; [4]1-X,1/2+Y,3/2-Z; [5]-X,1/2+Y,3/2-Z; [6]-1+X,1/2-Y,-1/2+Z; [7]1-X,-1/2+Y,3/2-Z; [8]-X,-1/2+Y,3/2-Z; [9]+X,1/2-Y,-1/2+Z

Table S4 The mechanical property of MMMs.

	F m (N)	σm (MPa)	εm (%)	E t (MPa)	εb (%)	F b (N)	σb (MPa)	U b (mJ)
1@PCL	4.10	1.02	48	7.64	68	1.30	0.325	20.2
1@PVDF	6.25	10.4	6.1	408	140	-0.0150	-0.0250	40.8

Table S5 The comparison of the detection limit between **1** and other reported chemical sensors for FA detection.

Materials	Detection limit (M)	Reference
Y_2O_3:Eu	0.083×10^{-6}	S4
CdTe	0.095×10^{-6}	S5
Carbon dots	1.2×10^{-6}	S6
ZnS: Mn or Cu	1.1×10^{-5}	S7
$CdInS_2$ QDs	8×10^{-5}	S8
1,10-phenantroline-Tb(III)-Ag NPs	0.21×10^{-6}	S9
MoS_2 QDs	0.1×10^{-3}	S10

Reference

[S1] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, Journal of Applied Crystallography, 2009, 42, 339-341.

[S2] G. Sheldrick, Crystal structure refinement with SHELXL, Acta Crystallographica Section C, 2015, 71, 3-8.

[S3] G. Sheldrick, A short history of SHELX, Acta Crystallographica Section A, 2008, 64, 112-122.

[S4] F. Gudarzy, A.B. Moghaddam, S. Mozaffari, *et al.* A lanthanide nanoparticle-based luminescent probe for folic acid. Microchim Acta 2013,180, 1257–1262.

[S5] P. Nagaraja, R.A. Vasantha. Spectrophotometric determination of folic acid in pharmaceutical preparations by coupling reactions with iminodibenzyl or 3-aminophenol or sodium molybdate–pyrocatechol. Anal Biochem 2002, 307, 316–321.

[S6] S.Y. Liu, J.J. Hu, X.G. Su Detection of ascorbic acid and folic acid based on water-soluble $CuInS_2$ quantum dots. Analyst 2012, 137, 4598–4604.

[S7] B. Zeng, F. Zhao. Single-walled carbon nanotube-ionic liquid paste electrode for the sensitive voltammetric determination of folic acid. Sens Actuat B 2008, 134, 895–901.

[S8] S.Q. Han, X.X. Chen. Copper nanoclusters-enhanced chemiluminescence for folic acid and nitrite detection. Spectrochim Acta A 2019, 210, 315–320.

[S9] Y. Ganjkhanlou, M. Kazemzad, F. Alikhani Hessari. Chromaticity dependence on Eu concentration in Y_2O_3:Eu nanopowders. Nano: Brief Report Rev 2010, 5, 111–116.

[S10] Y. Peng, W. Dong, L. Wan, *et al.* Determination of folic acid via its quenching effect on the fluorescence of MoS_2 quantum dots. Microchim Acta 2019,186, 605.