Support Information

Hydrogen-bond enhanced Tb/Eu-MOF visual detection for multiple trace fluoroquinolones in seawater and a portable 3D-printed sensor

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Text S1. Synthesis of (Tb)x(Eu)y-MOF@BTEC

The Eu^{3+} doping ratio in the material was optimized. Prepared (Tb)x(Eu)y-MOF@BTEC via a one-pot method. (Tb)x+(Eu)y =0.4mmol, with (Tb)x：(Eu)y ratios of 1:0, 72:1, 36:1, and 18:1 for low Eu doping. Take (0.40, 0.3945, 0.3892, or 0.3790 mmol) $Tb(NO_3)_3{\cdot}6H_2O$, (0, 0.0055, 0.0108, or 0.0210 mmol) $Eu(NO_3)_3{\cdot}6H_2O$, 0.3 mmol trimesic acid (H_3BTC), and 0.1 mmol 1,2,4,5-benzenetetracarboxylic acid (H_4BTEC) were ultrasonically dissolved in 5.7 mL DMF. Then, 34.3 mL ultrapure water was added and mixed. The final mixture was transferred to a reaction vessel, heated to 105°C, and maintained for 24 hours. Unreacted ligands and metal ions were sequentially removed by vacuum filtration using ethanol, water, and ethanol. After drying at 60°C for 5 hours, four Tb/Eu-BTC@BTEC composites with different Eu doping ratios were obtained.

Text S2. Synthesis of Ln - (H_3BTC)x (H_4BTEC)y

The H_4BTEC doping ratio in the material was optimized. Prepare Ln - (H_3BTC)x (H_4BTEC)y via a one-pot method. (H_3BTC)x+ (H_4BTEC)y =0.4mmol, (H_3BTC)x：(H_4BTEC)y = 1:0, 18:1, 9:1, and 3:1, with minor H4BTEC doping. Take 0.3892 mmol $Tb(NO_3)_3{\cdot}{}_6H_2O$, 0.0108 mmol $Eu(NO_3)_3{\cdot}{}_6H_2O$, (0.40, 0.3790, 0.36, or 0.3 mmol) trimesic acid (H_3BTC), and (0, 0.0210, 0.04, or 0.1 mmol) 1,2,4,5-Benzenetetracarboxylic acid (H_4BTEC) was ultrasonically dissolved in 5.7 mL DMF, followed by addition of 34.3 mL ultrapure water for mixing. The final mixture was transferred to a reactor, heated to 105° C, and maintained for 24 h. Unreacted ligands and metal ions were sequentially removed by vacuum filtration using ethanol, water, and ethanol. After drying at 60° C for 5 hours, four H4BTEC composites with different Ln - (H_3BTC)x (H_4BTEC)y ratios were obtained.

Text S3 Calculation of values for HOMO/LUMO

HOMO and LUMO energy levels were calculated using Gaussian 16W and GaussView 6.0 software. GaussView 6.0 was employed for molecular model construction, while Gaussian 16W was used for energy level calculations. Following model construction, structural optimization was performed to ensure full relaxation of all atomic positions until energy and force tolerances reached 1×10^{-5} eV and 0.03 eV/Å, respectively. Under these ground-state conditions, DFT calculations were performed on the molecular model, accounting for the influence of the dispersed system (seawater) on the HOMO and LUMO energy levels of the doped ligands (H_3BTC, H_4BTEC) and target antibiotics (FLE, NOR, ENR) within the material.

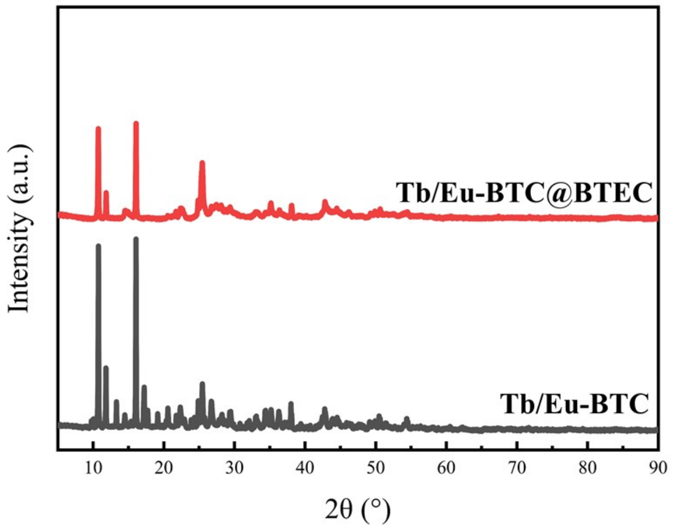

Fig. S1 XRD patterns of MOF material before and after H_4BTEC modification

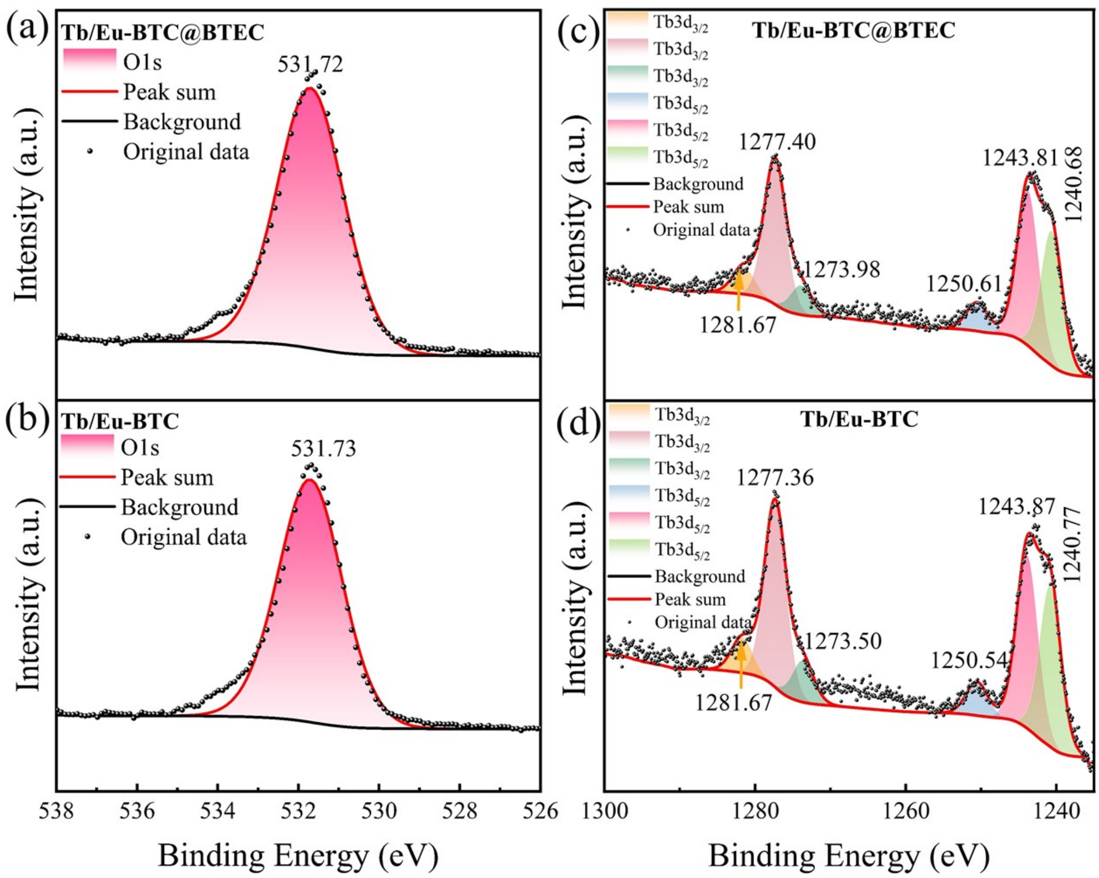

Fig. S2 (a)O1s spectra of Tb/Eu-BTC@BTEC and (b)Tb/Eu-BTC; (c) Tb3d spectra of Tb/Eu-BTC@BTEC and (d) Tb/Eu-BTC

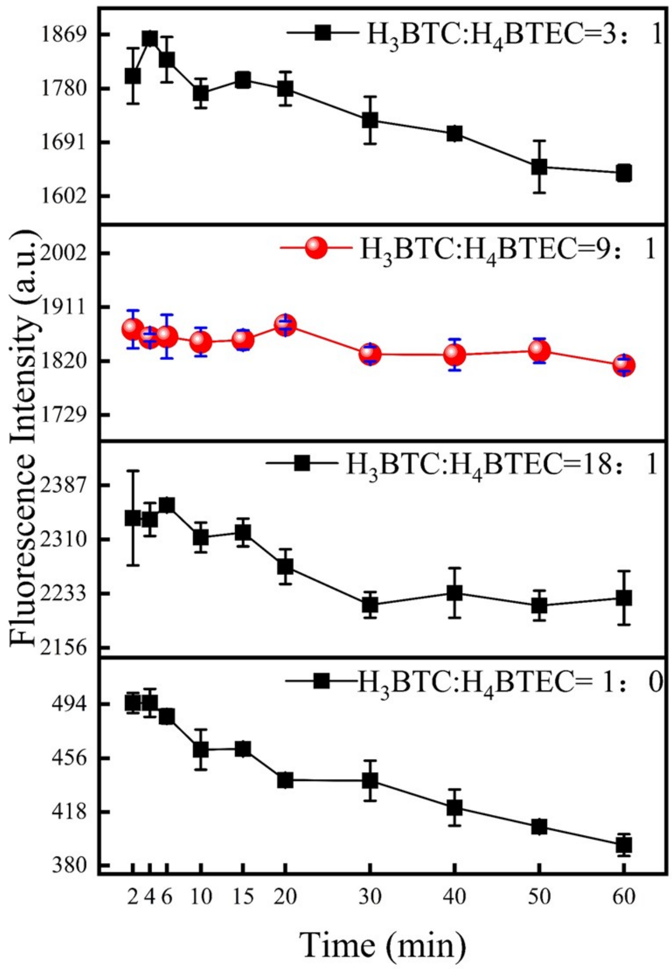

Fig. S3 Fluorescence stability of the material in simulated seawater over 60 minutes under varying H_3BTC:H_4BTEC ratios

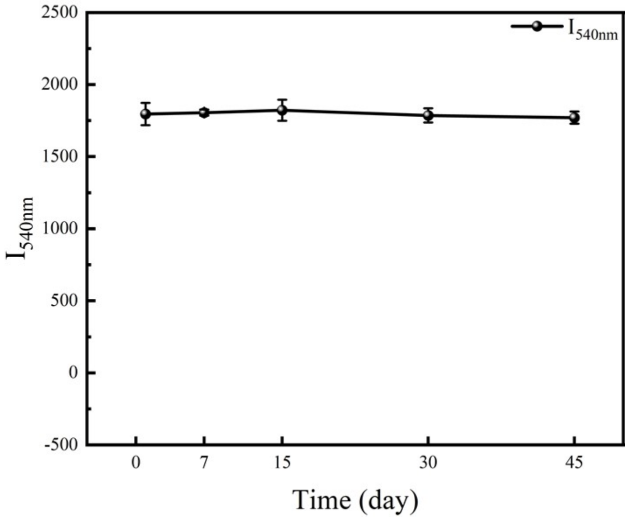

Fig. S4 45-day storage stability of Tb/Eu-BTC@BTEC

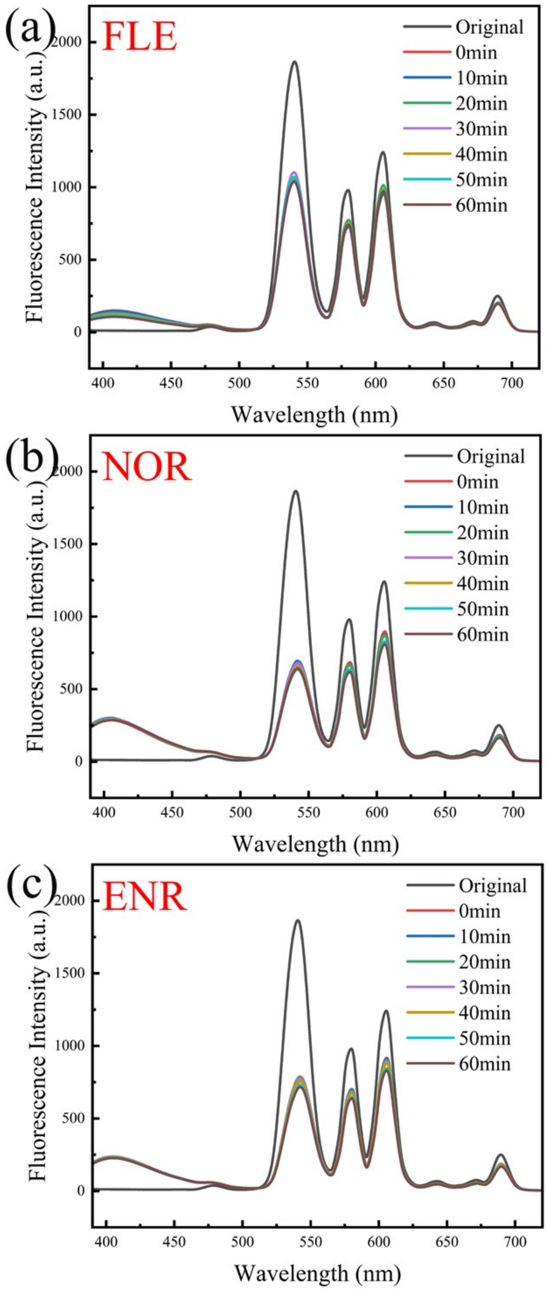

Fig. S5 Fluorescence change spectrum within 60 minutes after adding (a) FLE, (b) NOR, and (c) ENR to the dispersed system

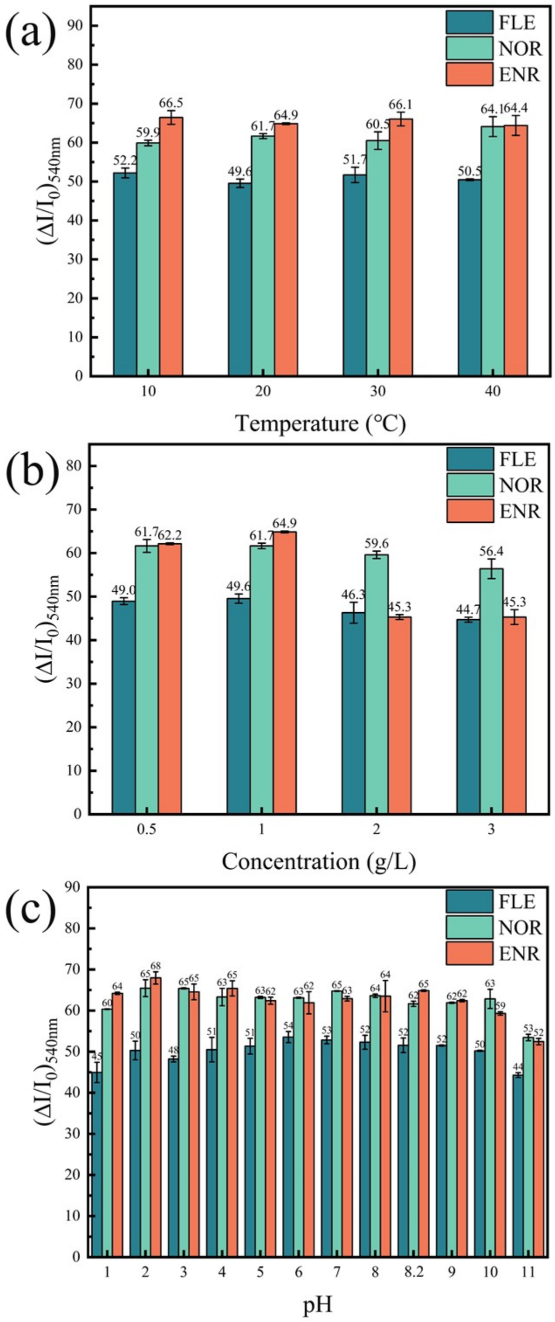

Fig. S6 Extinction rates of materials for FLE, NOR, and ENR at 540 nm under (a) different temperatures, (b) different dispersion concentrations, and (c) different pH conditions.

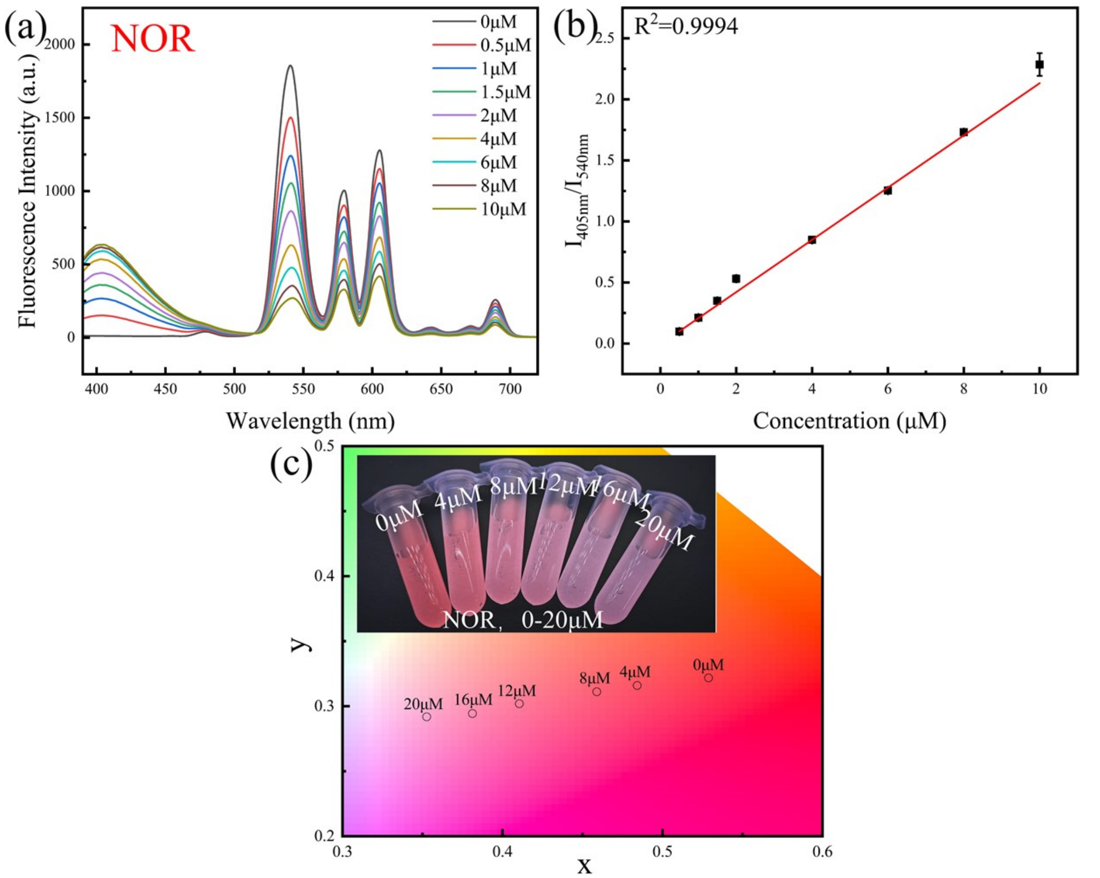

Fig. S7 Detection of NOR by Tb/Eu-BTC@BTEC in simulated seawater dispersion system ; (b) Linear relationship between I_{405nm}/I_{540nm} and NOR concentration; (c) Photograph and CIE diagram

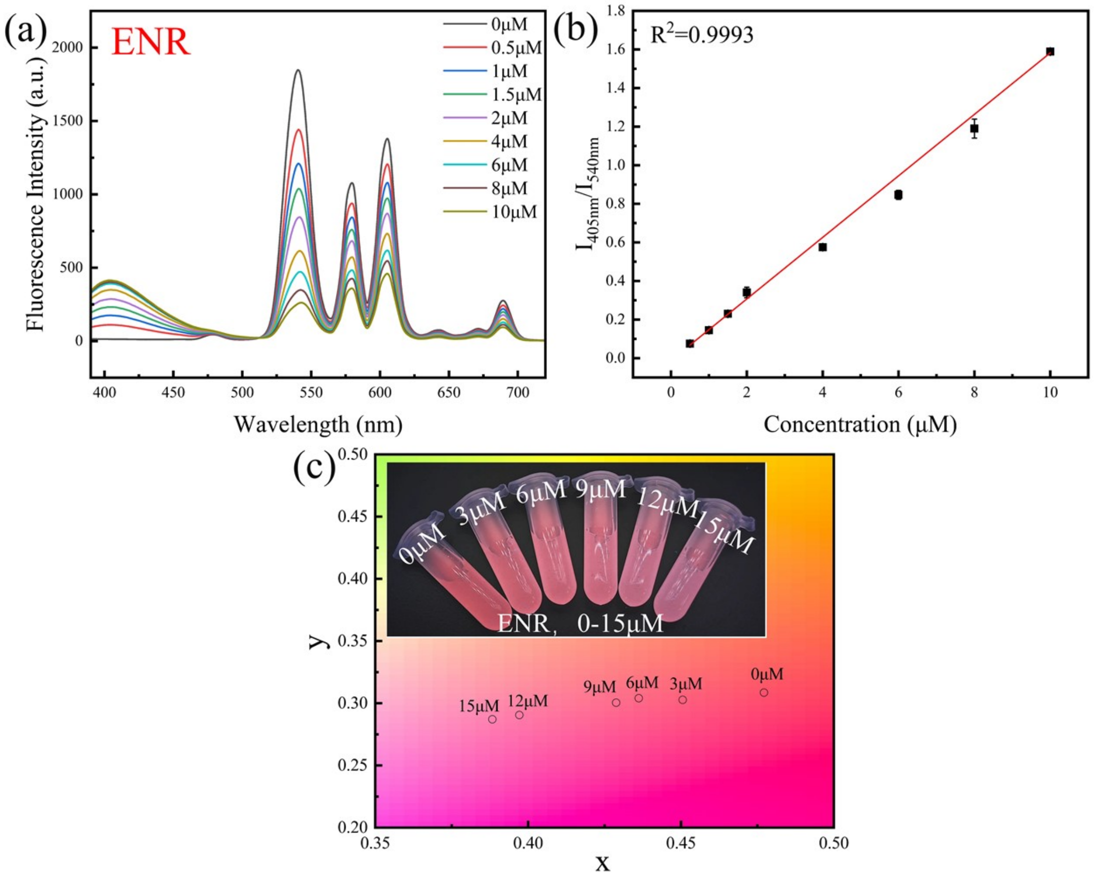

Fig. S8 Detection of ENR by Tb/Eu-BTC@BTEC in simulated seawater dispersion system ; (b) Linear relationship between I_{405nm}/I_{540nm} and ENR concentration; (c) Photograph and CIE diagram diagram

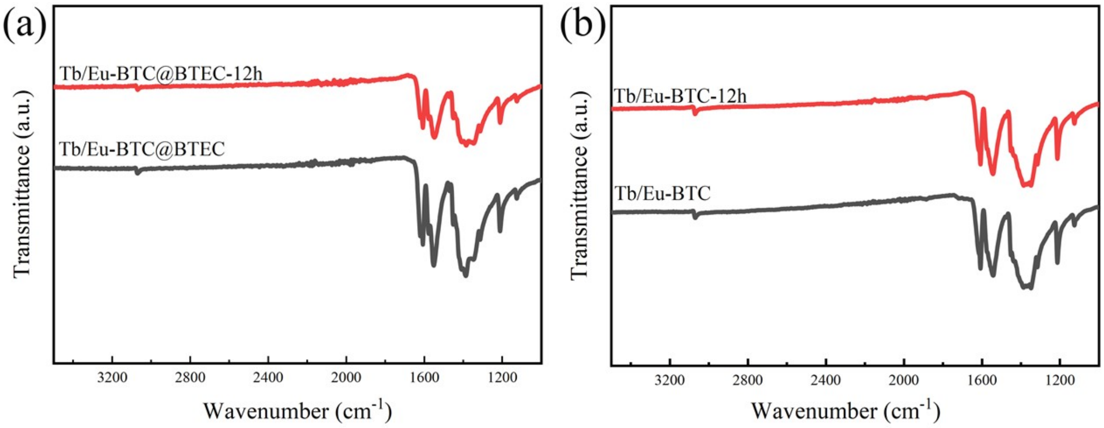

Fig. S9 FTIR spectra of (a) Tb/Eu-BTC@BTEC and (b) Tb/Eu-BTC before and after 12-hour seawater immersion treatment

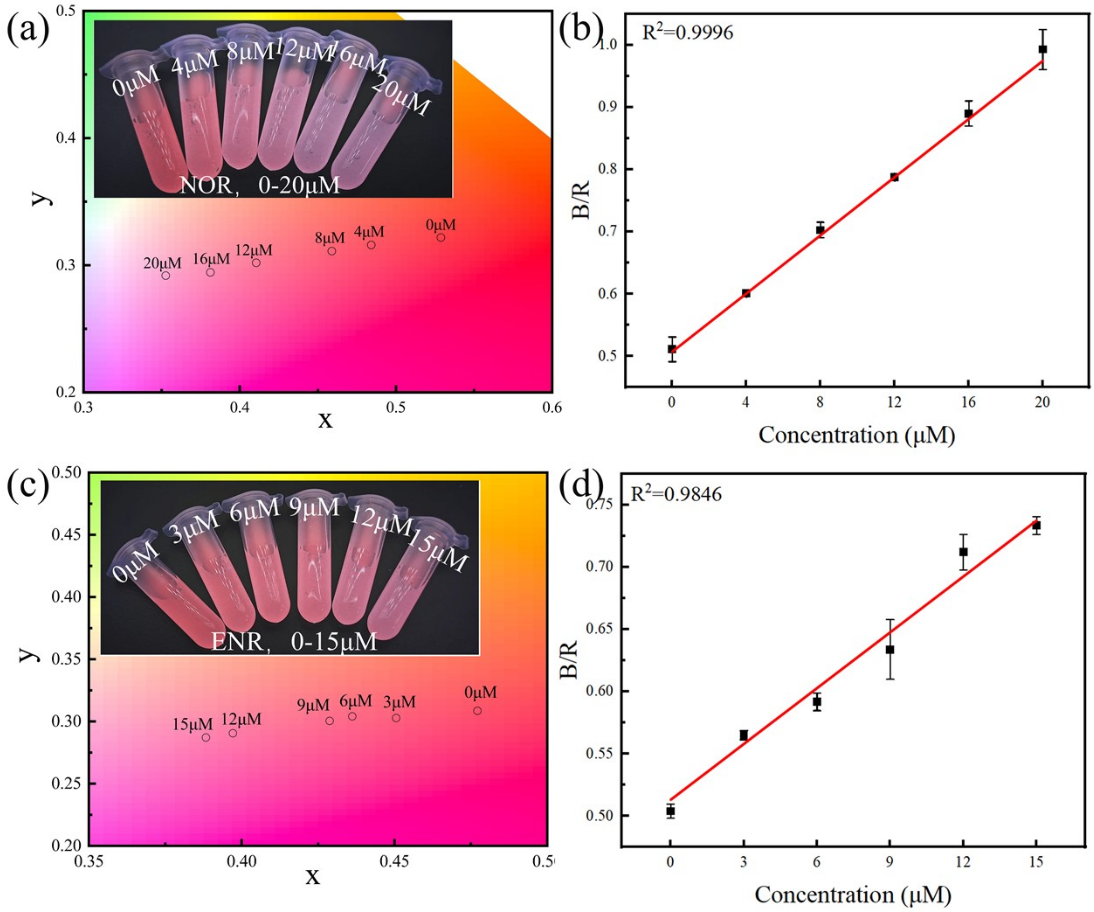

Fig. S10 (a) CIE diagram of 0–20 μM NOR detection in seawater samples, (b) Linear relationship between signal and NOR concentration; (c) CIE diagram of 0–20 μM ENR detection in seawater samples, (d) Linear relationship between signal and ENR concentration

Table S1 Simulating the chemical composition of seawater

Compuound	Concentration (g/L)
NaCl	24.53g/L
Na_2SO_4	4.094g/L
$MgCl_2 \cdot 6H_2O$	11.112g/L
$CaCl_2$	1.158g/L
$SrCl_2 \cdot 6H_2O$	0.042g/L
KCl	0.695g/L
$NaHCO_3$	0.201g/L
KBr	0.100g/L
H_3BO_3	0.027g/L
NaF	0.003g/L
$BaCl_2$	5.2mg/L
$Mn(NO_3)_2 \cdot 6H_2O$	5.4 mg/L
$Cu(NO_3)_2 \cdot 3H_2O$	3.9 mg/L
$Zn(NO_3)_2 \cdot 6H_2O$	1.51 mg/L
$Pb(NO_3)_2$	0.56 mg/L
$AgNO_3$	0.04 mg/L

Table S2 Initial parameters of two seawater samples

Sample name	Initial FLE concentration (μM)	Initial NOR concentration (μM)	Initial ENR concentration (μM)	pH
Seawater along the coast of Dalian, China	0	0	0	7.80
Seawater in a farming area in Dalian, China	0	0	0	7.69

Table S3 XPS survey data for the C1s energy level (atomic percentage)

Samples	Assignment	Peak BE	FWHM eV	Atomic(%)
Tb/Eu-BTC@BTEC (C1s)	π-π*	290.99	3.12	6.82
	O=C-O	288.64	1.58	24.52
	C-C	286.75	1.19	4.41
	C=C	284.80	1.75	64.25
Tb/Eu-BTC(C1s)	π-π*	289.77	3.37	10.14
	O=C-O	288.61	1.29	18.40
	C-C	286.72	3.37	31.03
	C=C	284.80	1.26	40.43

Table S4 Field-based ENR measurements of FLE and NOR using a portable device in the coastal waters of Dalian, China

Sample	Antibiotics	Concentration (μM)	Found (μM)	Recovery (%)	RSD (%, n = 3)
Seawater along the coast of Dalian, China	FLE	2	2.09	104.00	2.36
		6	5.61	93.16	3.51
		10	10.02	100.20	5.21
		12	12.64	105.33	5.94
	NOR	2	2.06	103.00	5.59
		6	6.51	108.50	2.50
		10	9.31	93.10	5.59
		12	13.21	110.00	2.49
	ENR	2	1.89	94.50	4.88
		6	6.22	103.67	0.55
		10	10.59	105.90	1.19
		12	11.57	96.41	2.94

Table S5 Field-based ENR measurements of FLE and NOR in seawater dispersion systems at a Dalian aquaculture zone, China using a portable device

Sample	Antibiotics	Concentration (μM)	Found (μM)	Recovery (%)	RSD (%, n = 3)
Seawater in a farming area in Dalian, China	FLE	2	1.94	97.00	2.56
		6	6.75	112.50	4.96
		10	10.40	104.00	0.92
		12	11.41	95.08	2.88
	NOR	2	2.07	100.35	2.22
		6	5.92	98.66	3.20
		10	9.89	98.90	1.43
		12	11.21	93.41	5.66
	ENR	2	1.97	98.50	4.21
		6	6.20	103.33	4.89
		10	11.64	116.40	3.74
		12	12.16	101.33	2.50