Supplementary Materials

Selective fluorescence detection of acetylsalicylic acid, succinic acid and ascorbic acid based on the responsive lanthanide metal fluorescent coordination polymer

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Materials and chemicals

Praseodymium nitrate ($PrN_3O_9·6H_2O$, 99%), cerium (III) nitrate hexahydrate ($CeN_3O_9·6H_2O$, 99.99%), dysprosium nitrate hexahydrate ($DyH_{12}N_3O_{15}$, 99.9%), neodymium (III) nitrate hexahydrate ($NdN_3O_9·6H_2O$, 99.0%), terbium nitrate pentahydrate ($Tb(NO_3)_3·5H_2O$, 99.9%), lanthanum (III) nitrate hydrate ($La(NO_3)_3·XH_2O$, 99%), samarium (III) nitrate hexahydrate ($SmN_3O_9·6H_2O$, 99.99%), gadolinium (III) nitrate hexahydrate ($GdN_3O_9·6H_2O$, 99%), europium nitrate pentahydrate ($EuH_{10}N_3O_{14}$, 99.9%), ethylene glycol (EG, 98%), fructose (99%), 2-aminoimidazole (2-AI, 97%), 2-ethylimidazole (2-EIM, 99%), and esterase (Est, from porcine liver, 15 U/mg) were purchased from Macklin Biochemical Technology Co., Ltd. (Shanghai, China). KCl, AA (≥99.0%), polyethylene glycol (PEG), and NaCl were purchased from Chengdu Chron Chemicals Co., Ltd. (Chengdu, China). $CaCl_2$ (≥96.0%),) was purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). Urea (99%) and sodium benzoate (99%) were purchased from Chongqing Chuandong Chemical Group Co., Ltd. (Chongqing, China). Creatinine (99%), vitamin B3 (VB3, 98%), rabbit plasma (with sodium citrate as the anticoagulant), 2-MIm (98%), 2-mercaptoimidazole (2-MI, 98%), and glucose (99%) were purchased from Shanghai YuanYe Biological Technology Co., Ltd. (Shanghai, China). The L-histidine (His, 99%), L (+)-arginine (Arg, 99%), and L-lysine (Lys, 99%) were purchased from Chengdu Huaxia Chemical Reagent Co., Ltd. (Chengdu, China). The L-cysteine (Cys, 99%) was purchased from Tianjin Guangfu Fine Chemical Co., Ltd. (Tianjin, China). Imidazole (IM, 99%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Xylose (99%) was purchased from Beijing Dingguo Biotechnology Co., Ltd (Beijing, China). Vitamin C tablet was purchased from Huazhong Pharmaceutical Co., Ltd. (Xiangyang, China). Aspirin Enteric-Coated

tablets were obtained from Bayer HealthCare Manufacturing Co., Ltd (Beijing, China). All the samples were deposited at the Pharmaceutical Engineering Laboratory at the School of Chemistry and Chemical Engineering, Chongqing University, Chongqing, China.

Instrumentation

Fluorescence analysis was carried out with an F-7100 fluorescence spectrophotometer (Hitachi, Tokyo, Japan). The tabletop low-speed centrifuge L420 was obtained from Hunan Xiang Yi Laboratory Instrument Development Co., Ltd. (Changsha, China). A water bath (HH-1S, Miqi Instrument Equipment Co., Ltd, Shanghai, China) was used in the temperature-controlling process. The field-emission scanning electron microscopy (SEM) (JSM-7600F, JEOL Ltd., Tokyo, Japan) was used to characterize the synthesized materials. The Fourier-transform infrared (FT-IR) spectra were recorded using a Nicolet iS50 (Thermo Scientific Inc., Massachusetts, USA). The sample's X-ray diffraction (XRD) patterns were acquired through an X' pert Powder diffractometer (Malvern Panalytical Ltd., Overijssel, Netherlands) with secondary beam graphite monochromated Cu Kα radiation. The Images and element composition of materials were obtained through transmission electron microscopy (TEM) (Thermo Fisher Scientific, Prague, Czechia). The ultrapure water used throughout this study was purified by a water purification system (ATSelem 1820A, Antesheng Environmental Protection Equipment, Chongqing, China). The ultrasonic cleaner was purchased from Kunshan Jielimei Ultrasonic Instrument Co., Ltd. (Kunshan, China).

Mass spectrometry analysis

All mass spectrometry (MS) experiments were performed on a QE Plus 21006403 mass spectrometer (Thermo Scientific Inc., Massachusetts, USA) equipped with standard ESI source. The reaction mixtures of ZIF-8/Est + ASA + 2-MIm + Dy (III), ZIF-8/Est

+ ASA + 2-MIm + Dy (III) + SA, and ZIF-8/Est + ASA + 2-MIm + Dy (III) + AA were analyzed by MS, respectively. 150 μL of ZIF-8 (concentration B) or Est (9.38 U/mL) and 150 μL ASA (0.50 or 0.75 mM) were mixed together in a 1.5 mL centrifuge tube and incubated at 40 ℃ for 3 min, then 300 μL 2-MIm (6.25 or 5.00 mM), 300 μL Dy (2.50 mM), and 300 μL ultrapure water (or 1.25 mM of SA, 0.75 mM of AA) were added to the above solution and incubated at 40 ℃ for another 3 min. Then, the solution after reaction was centrifugation for 1 min. Pass the supernatant through a 0.22 μm membrane and take 0.5 mL of supernatant for MS analysis (scan range: 50–1000 *m/z*). All analyses were conducted in a positive ion mode.

Supplementary Figures

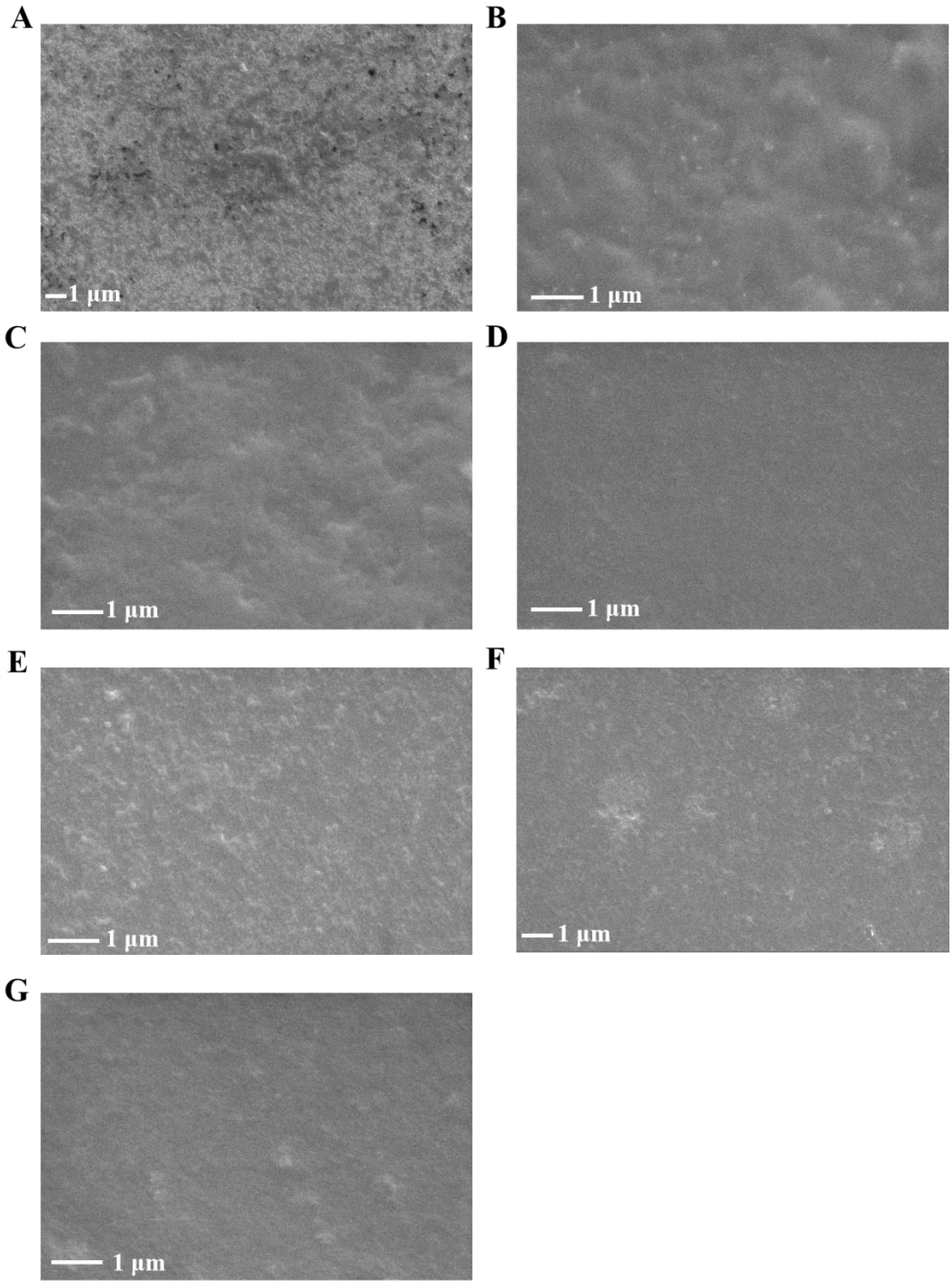


Figure S1 SEM images of the reacted solution (Est, ASA, 2-MIm, and Dy (III) (A), adding different SA concentrations of 0.16 mM (B), 1.25 mM (C), and 2.5 mM (D), adding different AA concentrations of 0.0078 mM (E), 0.13 mM (F), and 0.25 mM (G).

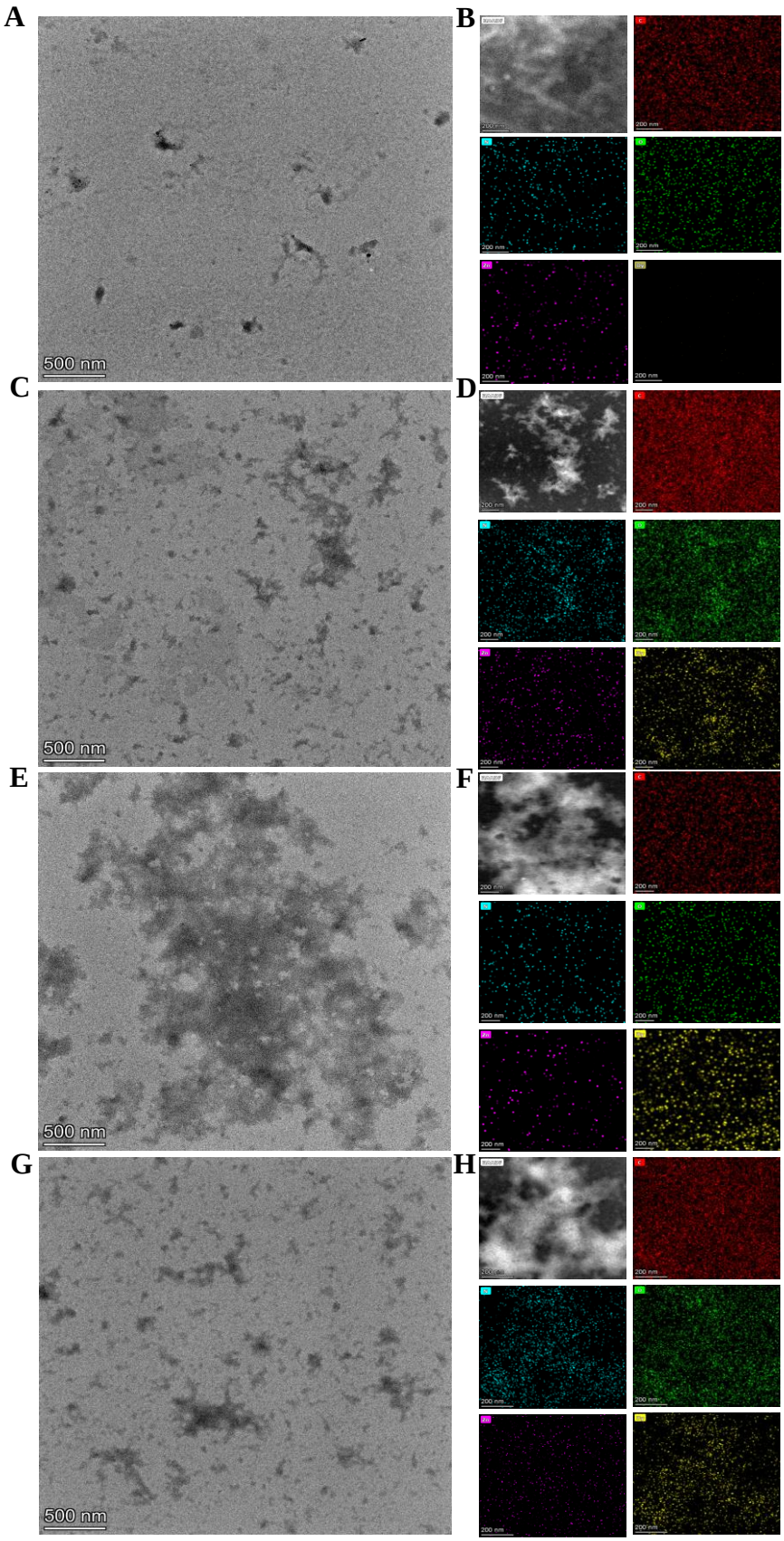


Figure S2 TEM images of Est solution (A), the reacted solution (Est, ASA, 2-MIm, and Dy (III)) (C), and adding SA (E) and AA (G), respectively. EDS analysis of Est solution (B), the above reacted solution (D), adding SA (F) and AA (H), respectively.

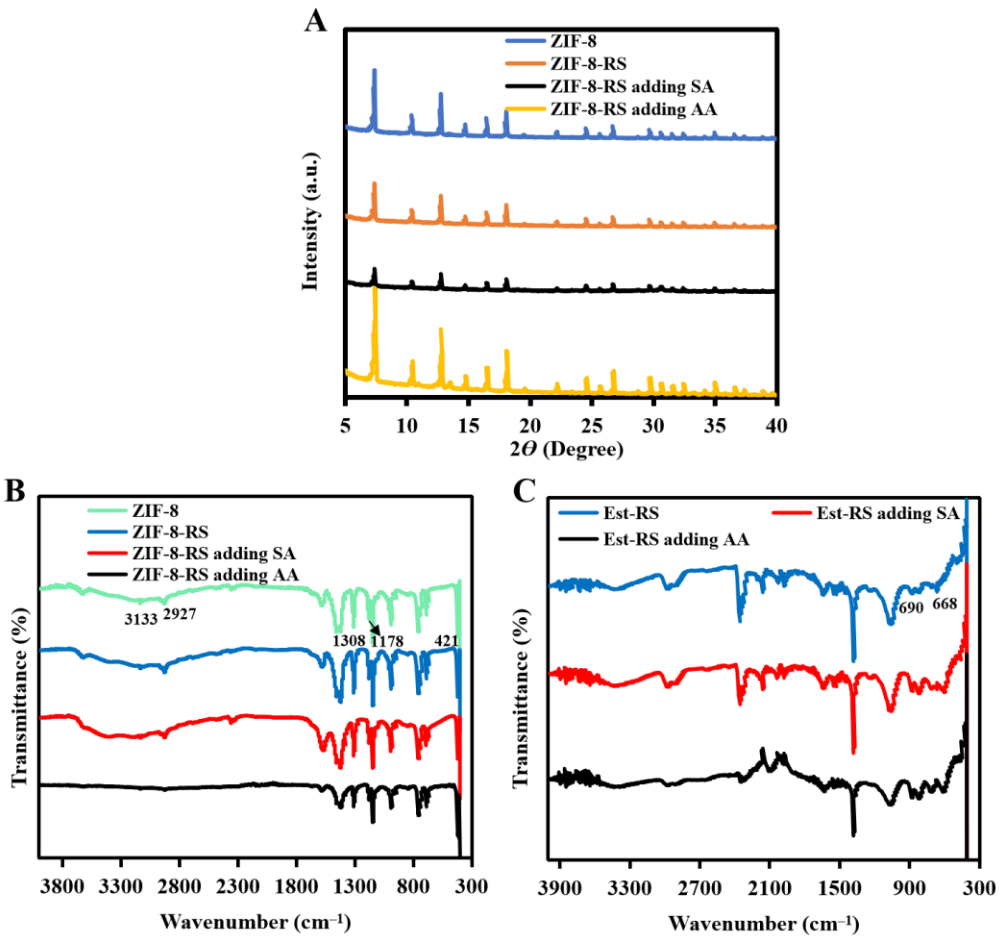


Figure S3 XRD analysis of the original ZIF-8, and its reaction solution (ZIF-8 + ASA + 2-MIm + Dy (III)) without and with adding SA and AA (A). FI-IR analysis of the original ZIF-8, and its reaction solution (ZIF-8, ASA, 2-MIm, Dy (III)) without and with adding SA and AA (B), the Est reaction solution (Est, ASA, 2-MIm, Dy (III)) without and with adding SA and AA (C). "RS" means reaction system.

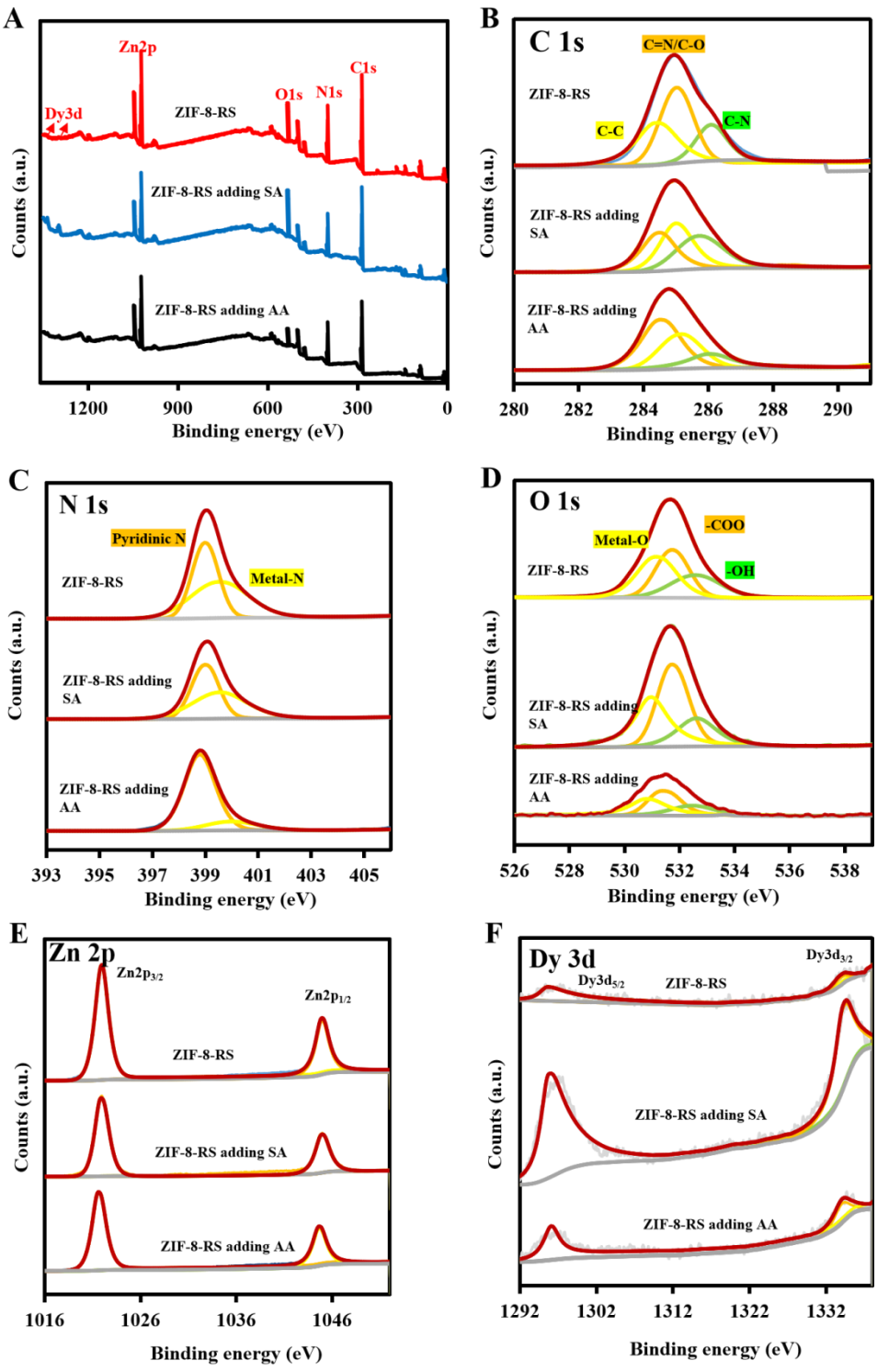
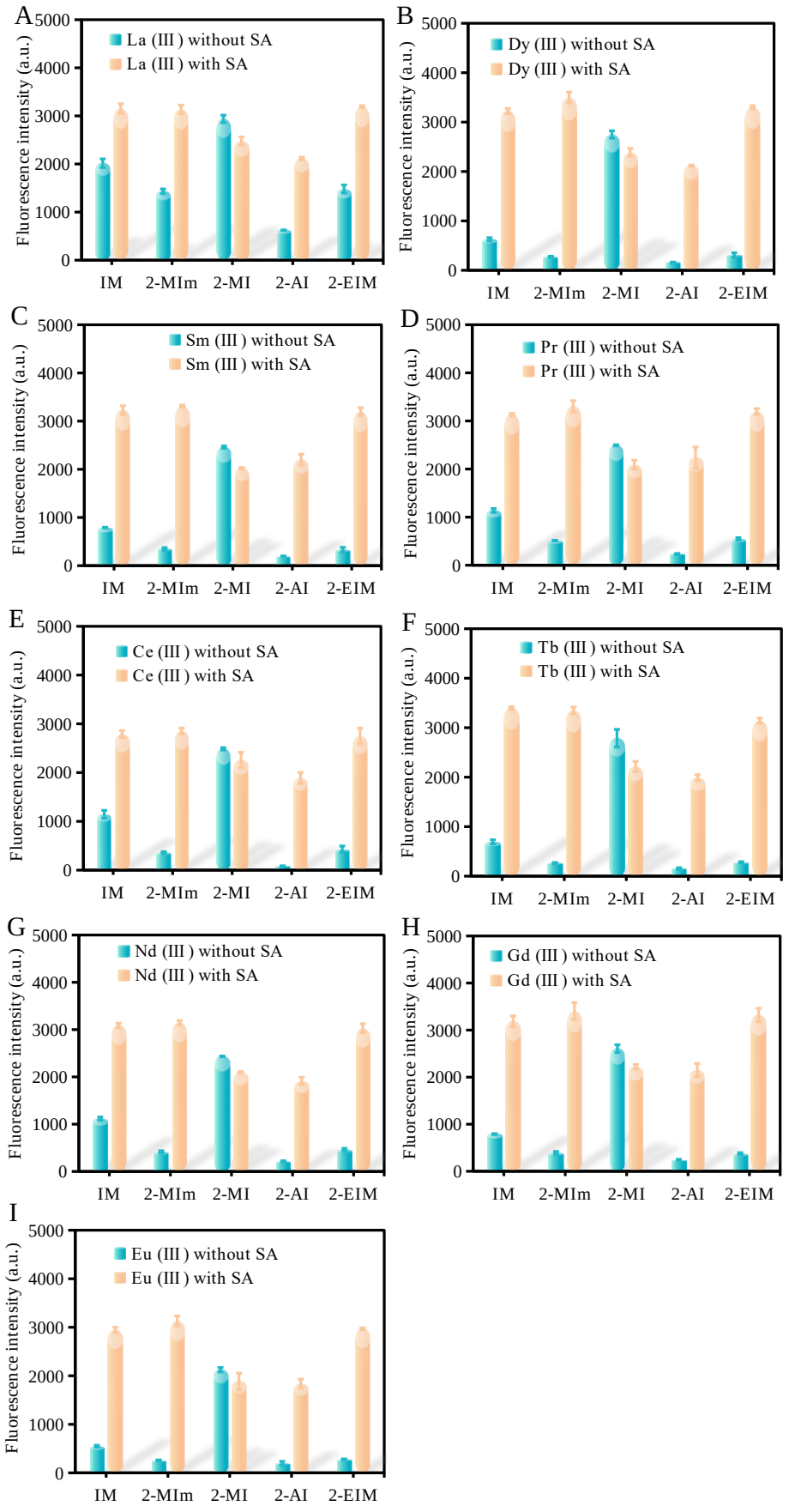


Figure S4 XPS analysis of the ZIF-8 reacted system without and with adding SA and AA. Survey scan (A), C 1s (B), N 1s (C), O 1s (D), Zn 2p (E), and Dy 3d (F). "RS" means reaction system.



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105 **Figure S5** Effects of different Ln (III) and imidazole ligands on Est-based reaction system.

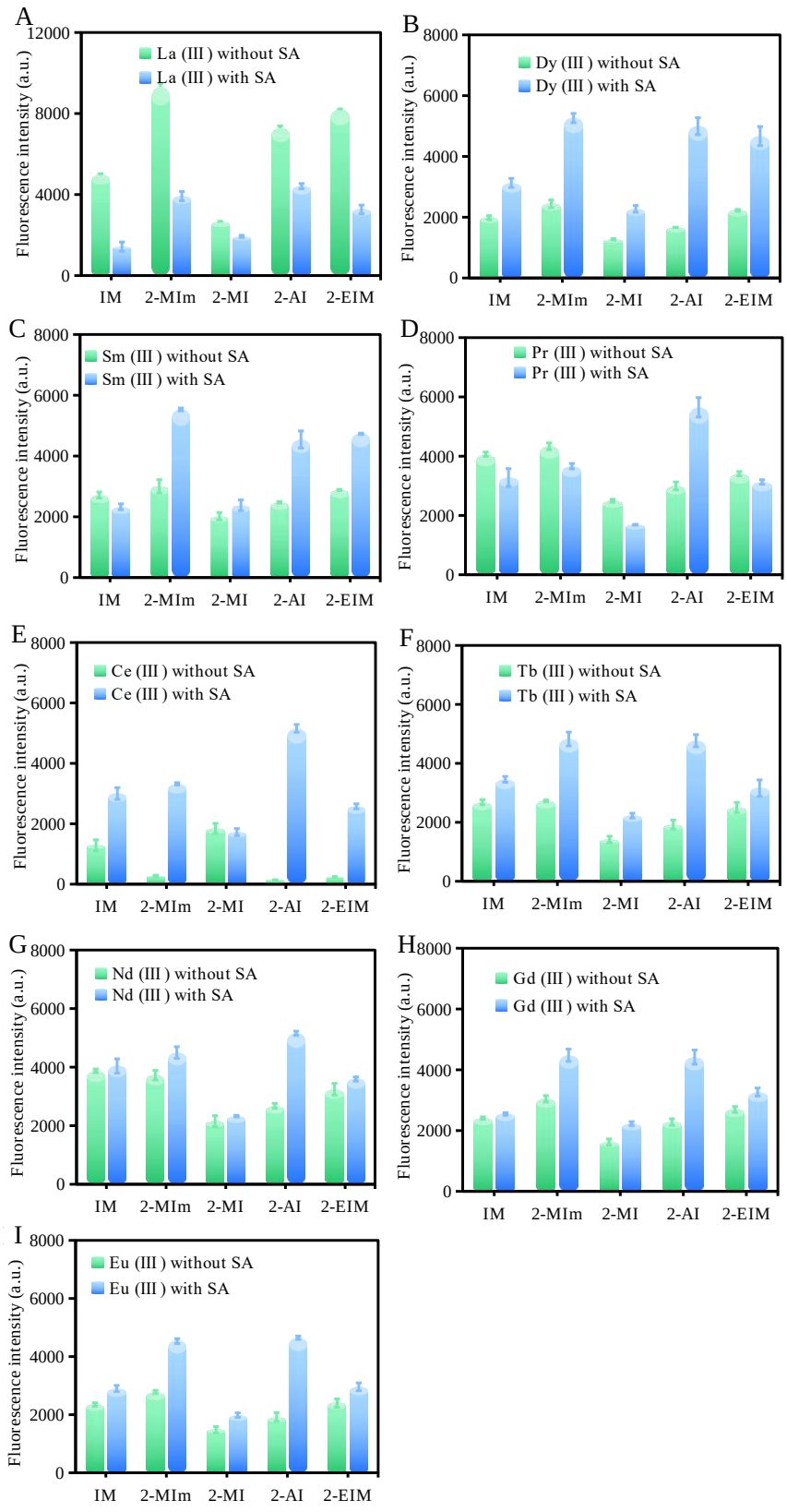


Figure S6 Effects of different Ln (III) and imidazole ligands on ZIF-8-based reaction systems.

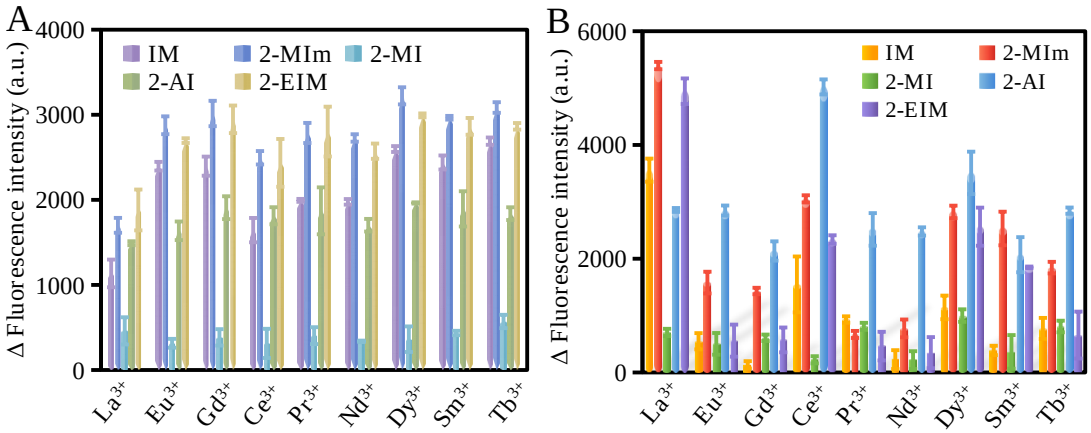


Figure S7 The Δ fluorescence intensity of different Ln (III) and ligands in Est (**A**) and ZIF-8 (**B**) reaction system.

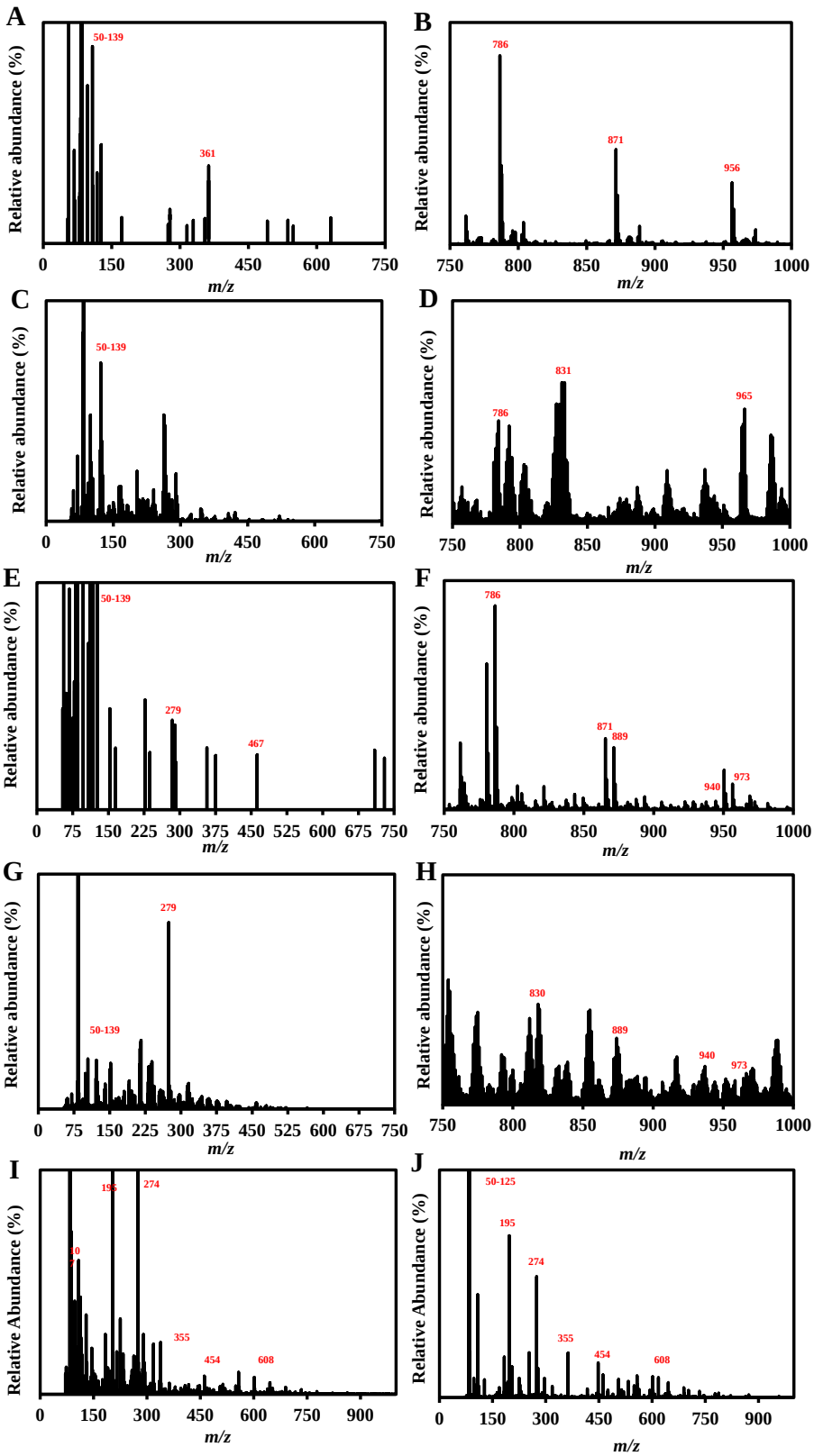


Figure S8 Mass spectra of the reaction mixtures of Est + ASA + 2-MIm + Dy (III) (A, B), ZIF-8 + ASA + 2-MIm + Dy (III) (C, D), Est + ASA + 2-MIm + Dy (III) + SA (E, F), ZIF-8 + ASA + 2-MIm + Dy (III) + SA (G, H), Est + ASA + 2-MIm + Dy (III) + AA (I), and ZIF-8 + ASA + 2-MIm + Dy (III) + AA (J), respectively.

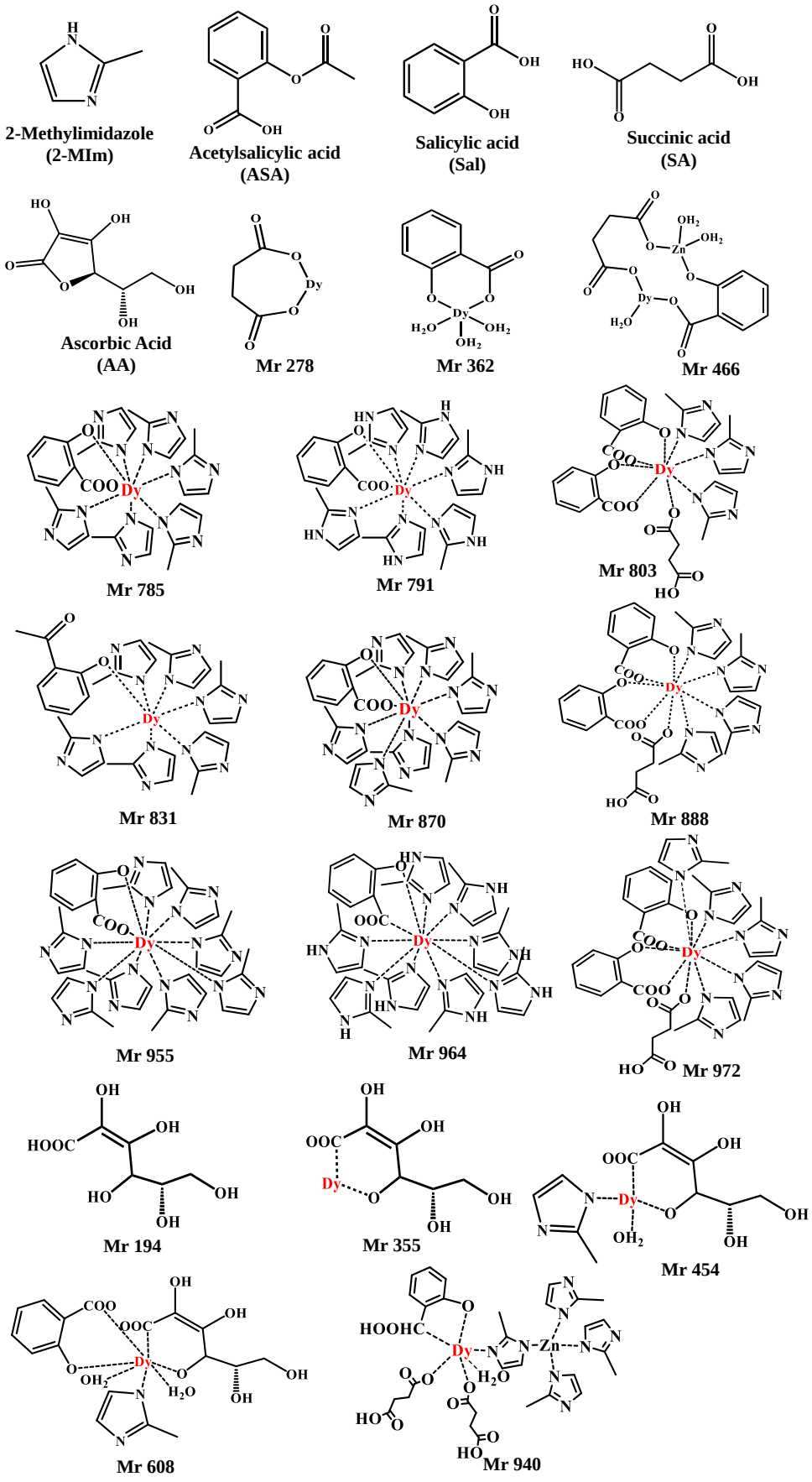


Figure S9 The chemical structures of tentatively identified compounds.

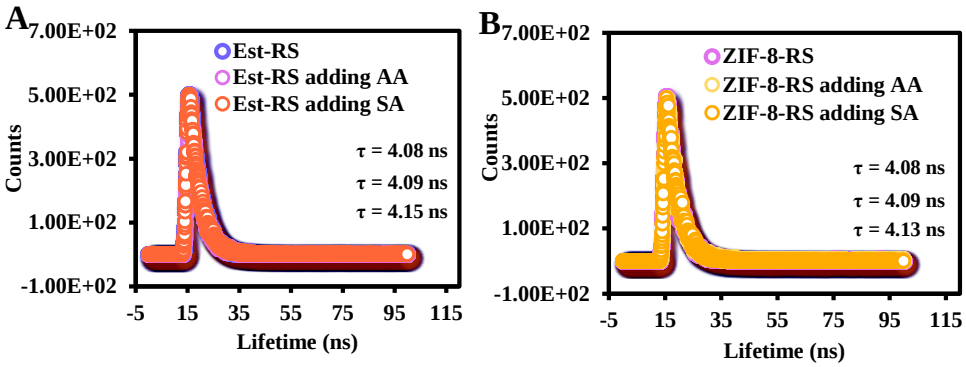


Figure S10 Time-resolved fluorescence spectra of Est (A) and ZIF-8 (B)-based reaction systems without and with adding SA and AA. "RS" means reaction system.

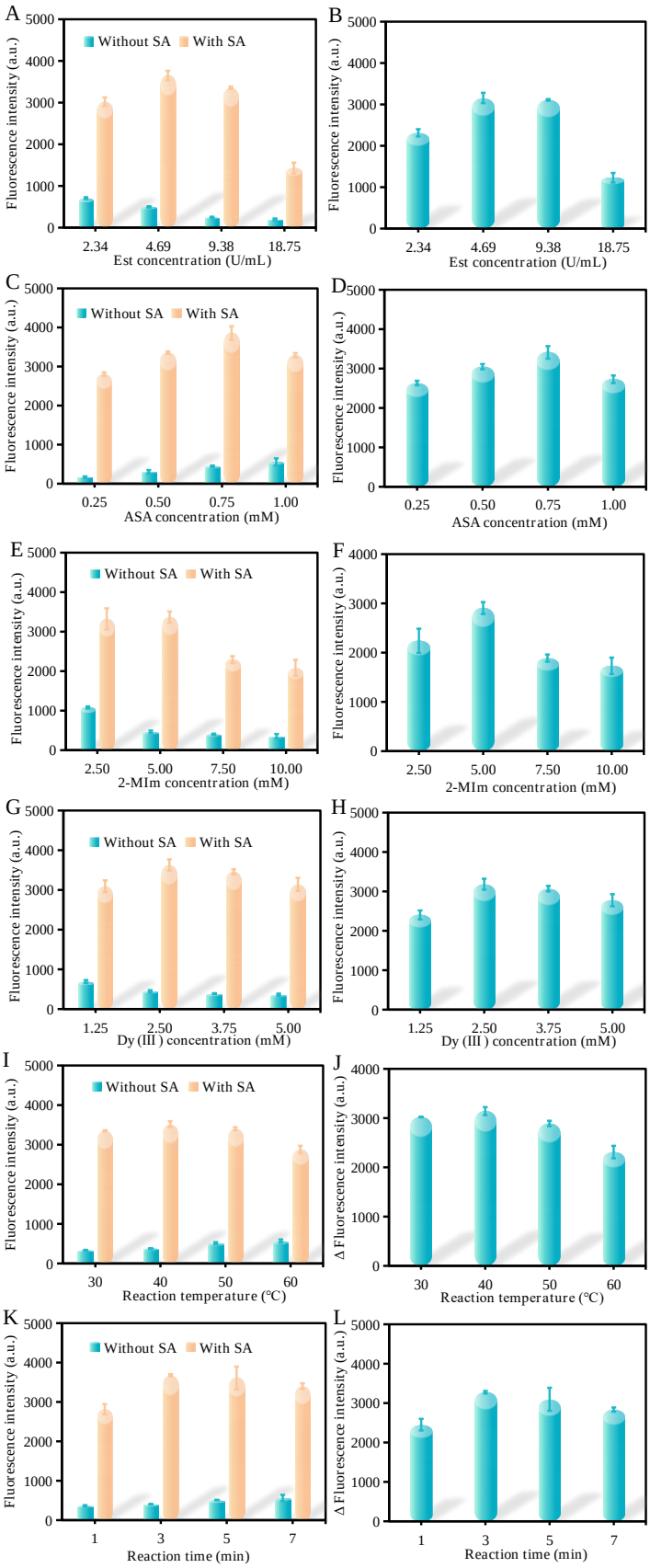
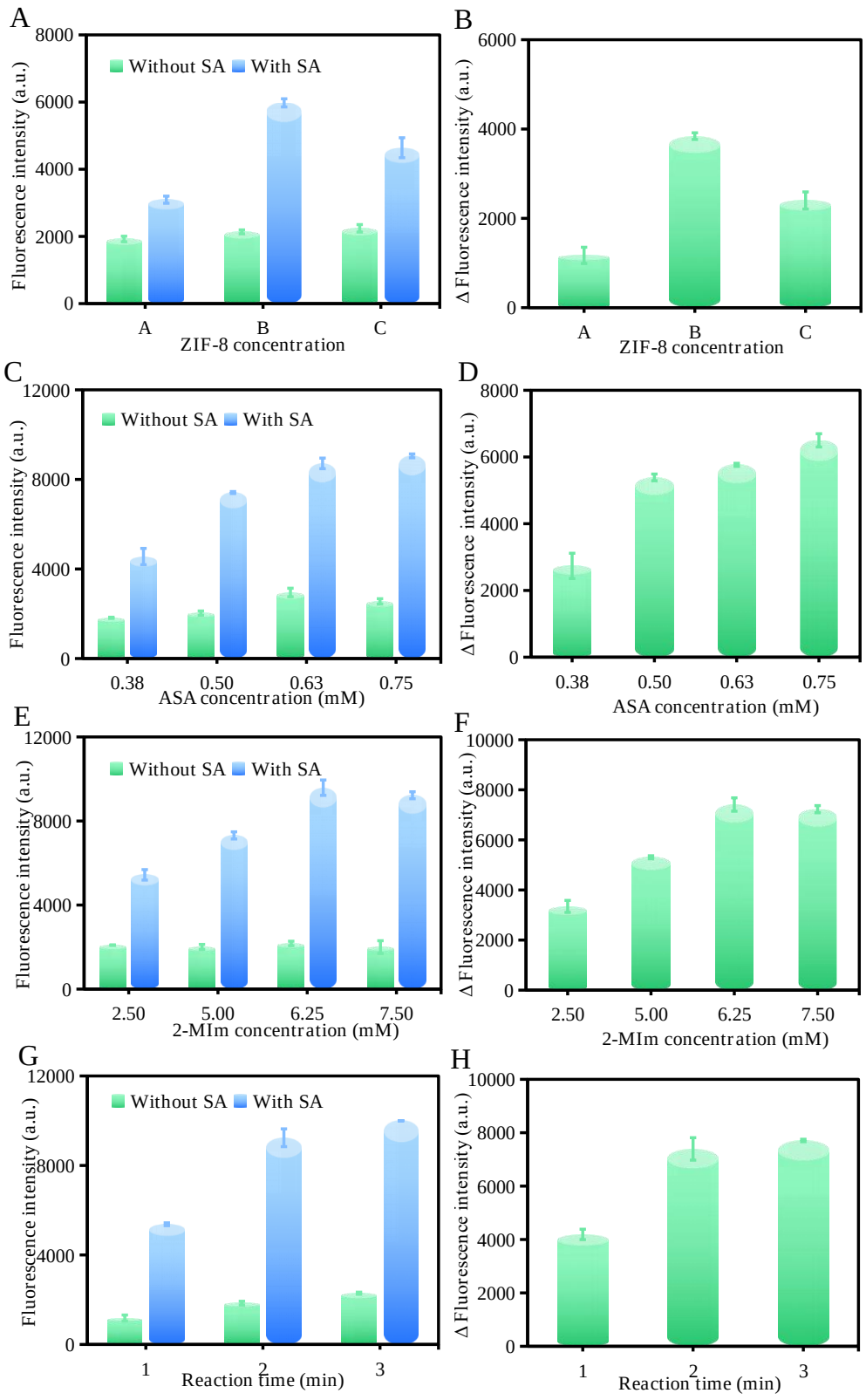


Figure S11 Effects of Est (**A**, **B**), ASA (**C**, **D**), 2-MIm (**E**, **F**), Dy (III) (**G**, **H**) concentrations, reaction temperature (**I**, **J**), and reaction time (**K**, **L**) on Est-based reaction system.



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127 **Figure S12** Effects of ZIF-8 (**A**, **B**), ASA (**C**, **D**), 2-MIm (**E**, **F**), and reaction time (**G**, **H**)

128 concentrations on ZIF-8 reaction system.

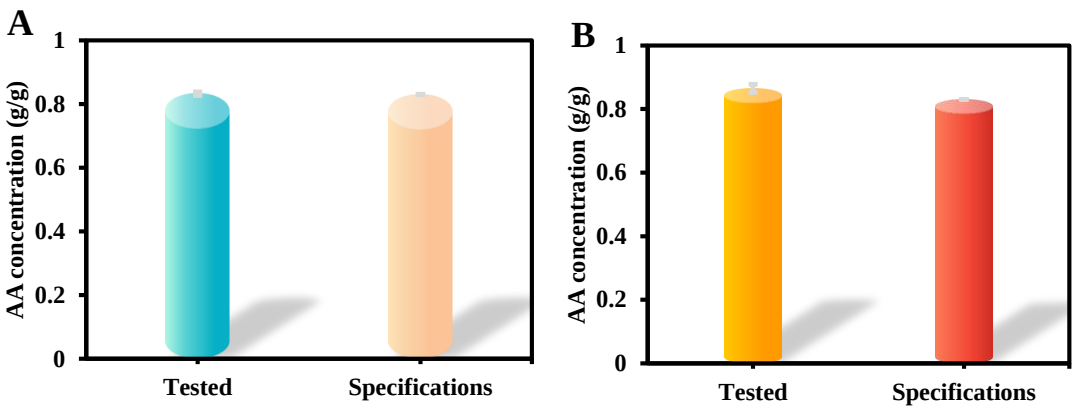

Figure S13 Determination of AA in vitamin C tablet (the specifications are shown for comparison) by Est (**A**) and ZIF-8 (**B**) reaction systems.

Table S1 Determination of ASA in Aspirin Enteric-Coated tablets.

	Specifications (mM)	Tested (mM)
ZIF-8	0.65	0.59 ± 0.01
Est	0.65	0.64 ± 0.01

Table S2 Determination of SA in rabbit plasma.

	Added (mM)	Found (mM)	Recovery (%)	RSD (%, $n = 3$)
ZIF-8	0.16	0.14	87.5	2.3
	1.25	1.07	85.6	4.4
	2.50	2.42	96.8	3.3
Est	0.078	0.068	87.2	2.1
	0.75	0.63	84.0	1.6
	1.50	1.48	98.7	0.1