Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Naked-Eye Detection of Hg(II) Ions by Visible Light-Induced Polymerization Initiated by a Hg(II)-Selective Photoredox Catalyst

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1. Materials Fluorescein sodium salt (**1**, > 97.5%, Sigma-Aldrich), hydrazine monohydrate (reagent grade, 98%), ethanol (extrapure, Daejung), *N*-vinylpyrrolidone (**3**, VP, Sigma-Aldrich), poly(ethylene glycol) diacrylate (**4**, PEGDA, Sigma-Aldrich), triethanolamine (**5**, TEOA, Sigma-Aldrich), agarose (low EEO, Sigma-Aldrich), $Hg(OAc)_2$ (> 98%, Sigma-Aldrich), NaCl (>99%, Sigma-Aldrich), $MgCl_2$ (>98%, Sigma-Aldrich), KCl (>99%, Sigma-Aldrich), $CaCl_2$ (>97%, Sigma-Aldrich), $Cr(NO_3)_3 \cdot 9H_2O$ (99%, Sigma-Aldrich), $MnCl_2$ (98%, Sigma-Aldrich), $FeCl_3$ (97%, Sigma-Aldrich), $CoCl_2$ (>98%, Sigma-Aldrich), $NiCl_2$ (98%, Sigma-Aldrich), $CuCl_2$ (99%, Sigma-Aldrich), $ZnCl_2$ (>98%, Sigma-Aldrich), $CdCl_2$ (Sigma-Aldrich), slide glass (Marienfel-superior), visible LED (wavelength: 520-525 nm, 50 W, luminous flux: 4000-4500, YXO YUXINOU, Shenzhen, China), adhesive black PVC film (CSH-3800, Samhyeob Tape Co., LTD, South Korea), and deionized water (18.2 MΩ·cm, Milli-Q® Direct Water Purification System, Merck Millipore) were purchased and used without further purification.

2. Experimental details

2.1 Experimental procedures

Synthesis of 2-amino-3′,6′-dihydroxyspiro[isoindoline-1,9′-xanthen]-3-one (fluorescein hydrazide, (1). Fluorescein hydrazide was synthesized following a procedure described in the literature.[1] The excess of hydrazide monohydrate was slowly added into a mixture of fluorescein (0.3 g, 1 mmol) dissolved in ethanol (20 mL) at room temperature. After stirring at 80 °C for overnight, the solvent was removed under a reduced pressure. The crude product was purified by recrystallization with water, filtered, and then dried under a reduced pressure to afford as a pale yellow powder (219 mg, 63% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.8 (2H, s), 7.77 (1H, m), 7.49 (2H, m), 6.99 (1H, m), 6.59 (2H, d, J = 2.5 Hz), 6.46 (2H, dd, J =

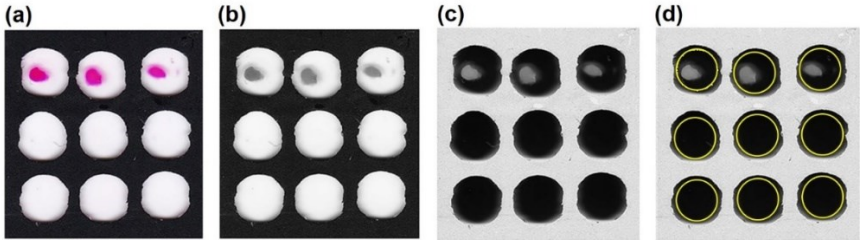
8.6, 2.5 Hz), 6.40 (2H, d, J = 8.6 Hz), 4.38 (2H, s); ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.94, 158.67, 152.88, 151.99, 133.07, 129.82, 128.87, 128.42, 123.90, 122.82, 112.47, 110.43, 102.83, 65.09. MS (MALD-ToF, matrix: 3-hydroxypyridine-2-carboxylic acid): m/z = 347.59 $[M+H]^+$ (cal. 346.09 $[M]^+$)

Preparation of a chip. The agarose film-coated glass surface was prepared following a procedure described in the literature.[2] An agarose solution (0.2 wt% in water) was prepared by dissolving agarose power in hot water (100 °C) for 2 min. Subsequently, the agarose solution (2 mL) was carefully dropped onto a bare glass slide, which had been cleaned by using an oxygen-plasma cleaner (Harrick, PDC-32G), until the mixture solution spread evenly to all edges of the glass (size: 2.5 × 7.5 cm). As the water evaporated, the agarose film slowly formed on the glass surface after passing through a gel phase. The agarose film was covered by an adhesive black PVC film (CSH-3800, Samhyeob Tape Co., LTD, South Korea), containing holes produced by a hole puncher (Peace Korea, Co., LTD). Each chip had nine holes, and the diameter of each hole was about 0.6 cm.

Interfacial photopolymerization. We mixed compound **1** (1 mM) and Hg(II) acetate (1 equiv.) in 100 μL of ethanolic aqueous solution and reacted at room temperature for 15 min. After the resultant solution was diluted in water, the diluted solution (2 μL) was spotted on the agarose film using a micropipette. The spotted chip was characterized by a fluorescence scanner, and fluorescence intensity was analyzed by imageJ software. After the characterized chip was kept in a dark room for overnight, we dropped 10 uL of the stock solution, containing VP (**3**, 400 mM), PEGDA (**4**, 600 mM), triethanolamine (**5**, 750 mM) and an enhancer (eosin

Y, 120 nM) on each spot region (diameter: 0.6 cm). The interfacial photopolymerization was carried out for 1 min under the visible LED at aerobic conditions. After the photopolymerization, the chip was stained with eosin solution (50 mM in water) for 3 min, and then carefully washed with water (about 20 mL) to remove the excess staining solution. The stained chip was imaged by a photo canner (CanoScan LiDe 300, Cannon)

Analysis of Colorimetric intensity. The colorimetric intensity was determined by ImageJ software (downloaded from the NIH website) and the procedure is as follows. After the photopolymerization and staining process, (a) the resulting chip was captured by a photo scanner, generating a RGB image, and (b) ImagJ software converted the obtained RGB image to a 16-bit gray-value image, which can adjust the intensity values from 0 to 65535. (c) The 16-bit grayscale image was inverted using "Edit-Invert" function in the software, and (d) anaylsis was performed on 80% of the entire hole area, in which the yellow circles in the image (d) indicated the selected areas for the analysis.



Photopolymerization in a single-phase solution. We mixed compound **1** (1 mM) with the interfering metal ions (1 equiv.) and Hg(II) acetate (0.1 equiv.) in 100 μL of ethanolic aqueous solution in a glass vial (volume: 5 mL). After 15 min at room temperature, we added 250 μL of the stock solution, containing **3** (400 mM), **4** (600 mM) and **5** (750 mM) into the reaction

mixture. After visible LED exposure for 1min under aerobic conditions, the resulting solution was stained with phenolphthalein (1 mg) naphthalene and NaOH (1 mg) for visualization. For control experimental, compound **1** (1 mM) was mixed with the interfering metal ions (1 mM) in the glass vial for 30 min at room temperature. The photoplymerization and staining process were carried out the same condition as we did.

2.2 Characterizations

Fluorescence scanner. Fluorescence images of the chip were obtained using a SensoSpot® Fluorescence Microarray Analyzer (Sensovation AG, Radolfzell, Germany) at a wavelength of λ=528 nm (exposure time: 150 ms). The obtained fluorescence images were analyzed by ImageJ software (National Institutes of Health, 6 Bethesda, Maryland, USA).

UV/Vis and fluorescence spectrophotometer. The excitation spectra were obtained by using a UV-Vis spectrophotometer (Shimadzu, UV-1800). The emission spectrum were obtained by fluorescence spectrophotometer (Jasco, FP-6500).

Matrix-assisted laser desorption ionization-time of flight (MALDI-ToF). Mass analysis was performed with Axima LNR MADLDI-ToF (Shimadzu, Japan) at the Bioneer Corporation (Daejeon, South Korea). A dried sample was mixed with 10 μL of matrix solution (3-hydroxypyridine-2-carboxylic acid, 50 mg/mL in pure water). The resulting solution was dropped on a template and then dried under vacuum. The detailed conditions were as follows. Analysis mode: linear mode, laser repetition rate: 10 Hz, number of shot: 10 shots, polarity: positive, deflection: off, voltage: 20 kV (ion source), 6.2 kV (lens), and 2.6-3.4 kV (liner detector).

2. Supporting figures

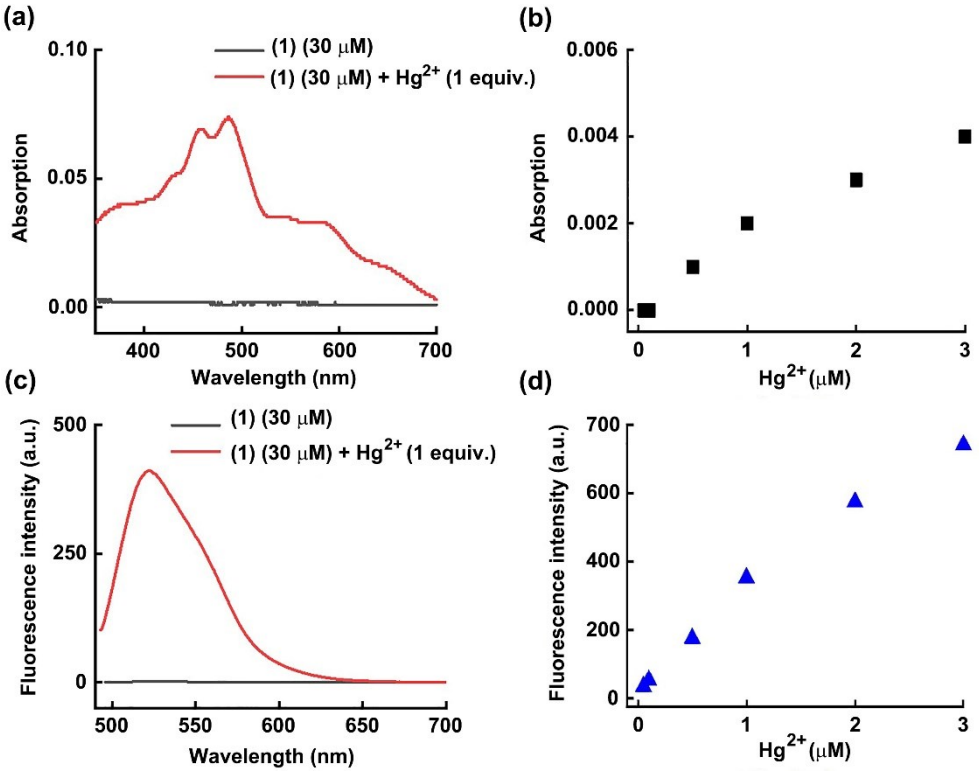


Fig. S1 (a) UV-Vis absorption spectra of **1** (30 μM) and **1** with mercury(II) acetate (1 equiv.) in aqueous solution (ethanol: water =50:50, v/v), (b) a plot of absorbance versus various concentrations of a reaction mixture, (c) emission spectra of **1** (30 μM) and **1** with mercury(II) acetate (1 equiv.) in aqueous solution (ethanol: water =50:50, v/v), (d) a plot of fluorescence intensity versus various concentrations of a reaction mixture.

Table S1 Photophysical the properties of (**1**)**,** (**2**), and fluorescein.[a]

Compound	λ_{max} (nm)	ε ($cm^{-1}\cdot M^{-1}$)	λ_{em} (nm)	Φ_f
(1)	225	58100	N.A	N.A
(2)	506	6500	530	0.38[b]
Fluorescein	498	37000	521	0.87[b]

[a] The photophysical data were measured in ethanol.

[b] Rhodamine 6G was used as a standard, and the relative quantum yield was determined from IUPAC technical report.[3]

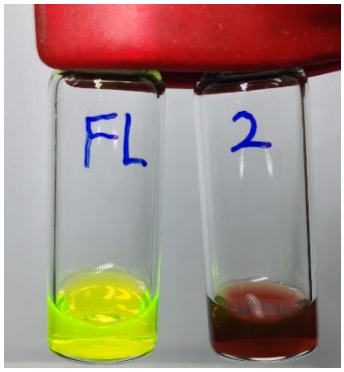


Fig. S2 The photo images of fluorescein (FL) solution (1 mM in ethanol) (left) and reaction mixture (**2**) (1 mM in ethanol) (right).

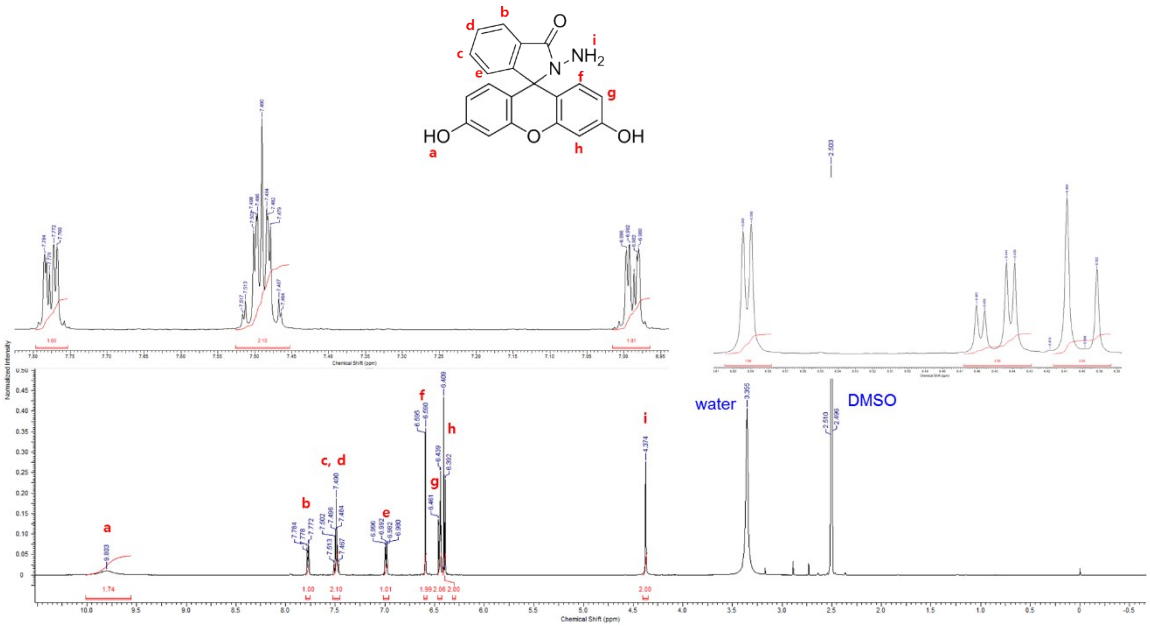


Fig. S3 ^{1}H-NMR spectrum of fluorescein hydrazide (**1**).

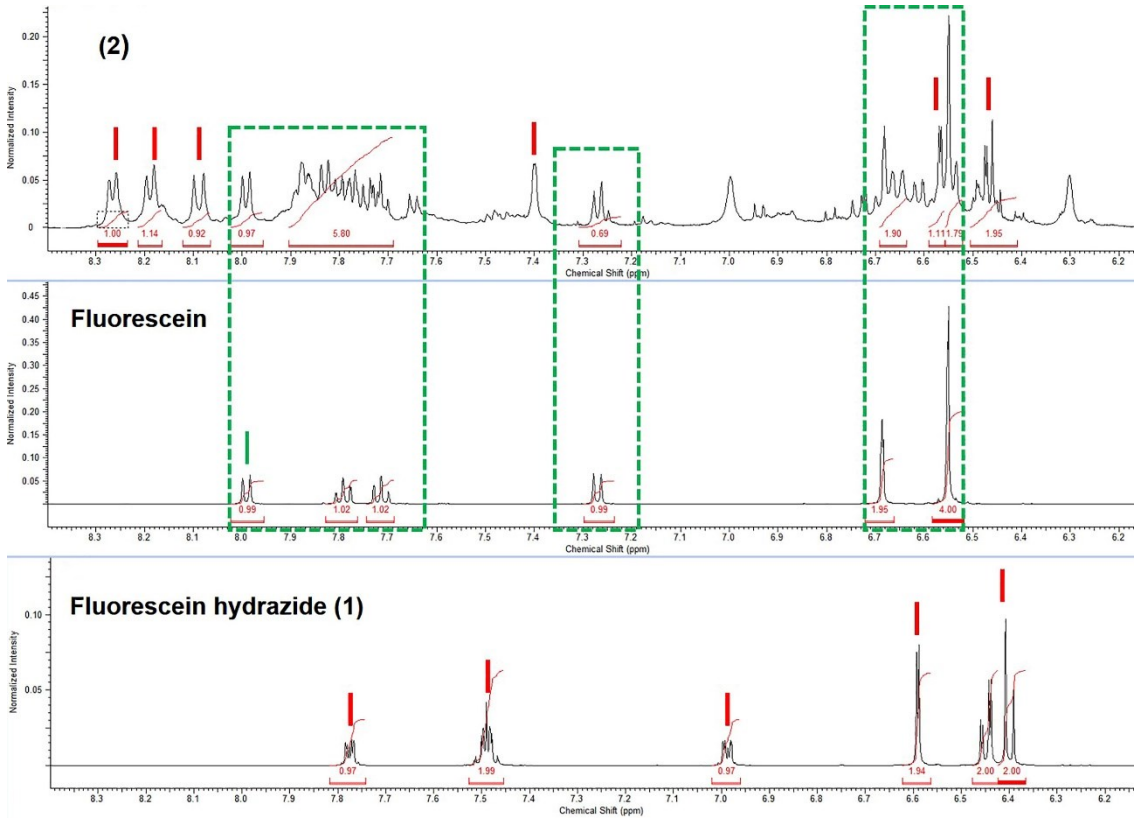


Fig. S4 ^{1}H-NMR spectra of (2), fluorescein, and fluorescein hydrazide (1).

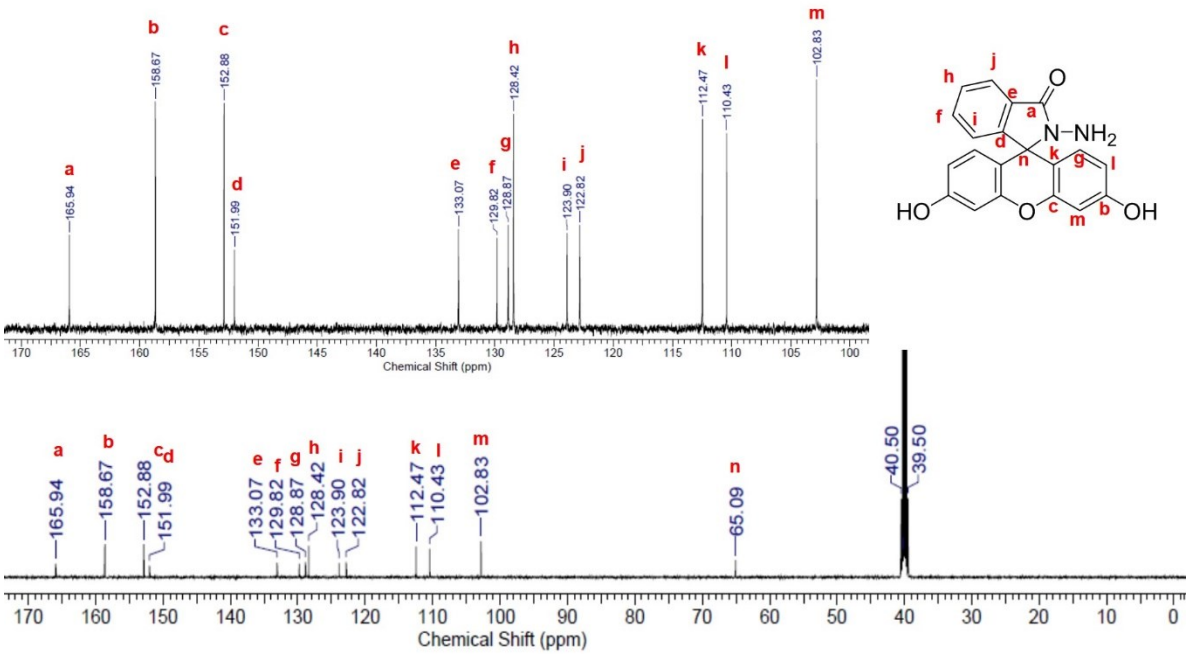


Fig. S5 ^{13}C-NMR spectrum of fluorescein hydrazide (**1**).

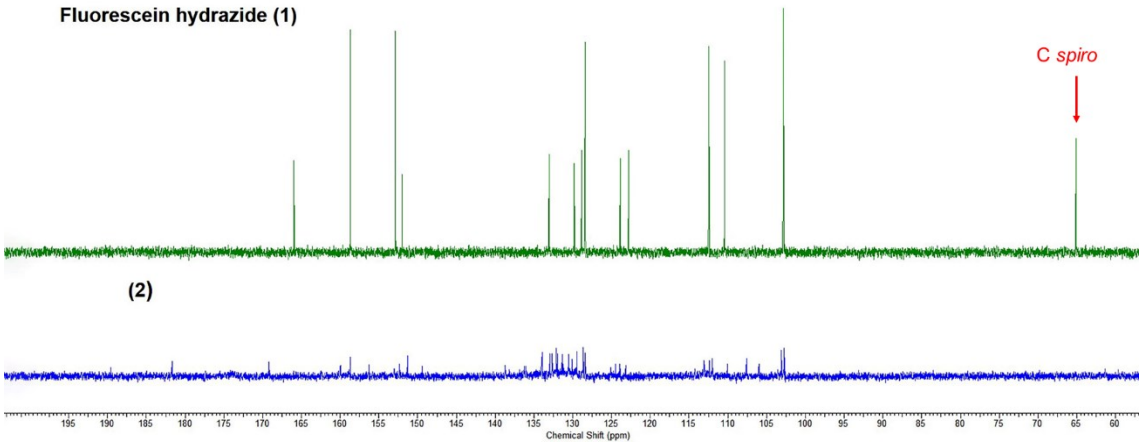


Fig. S6 ^{13}C-NMR spectra of fluorescein hydrazide (**1**) and (**2**).

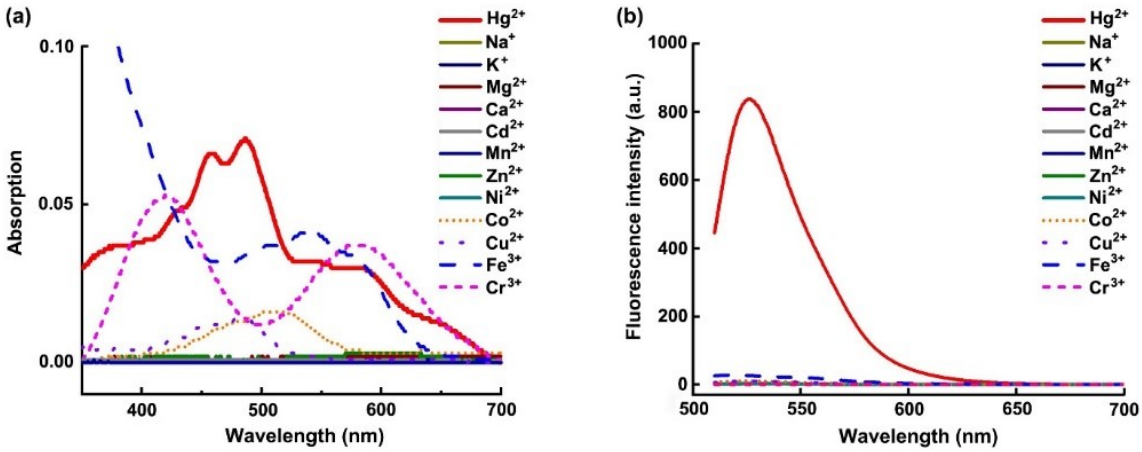


Fig. S7 (a) UV-Vis absorption spectra of **1** (30 μM) after the addition of mercury(II) acetate (1 equiv.) and each other interfering metal ion (100 equiv.) in aqueous solution (ethanol: water =50:50, v/v), and (b) emission spectra of **1** (30 μM) after the addition of mercury(II) acetate (1 equiv.) and each other interfering metal ion (100 equiv.) in aqueous solution (ethanol: water =50:50, v/v)

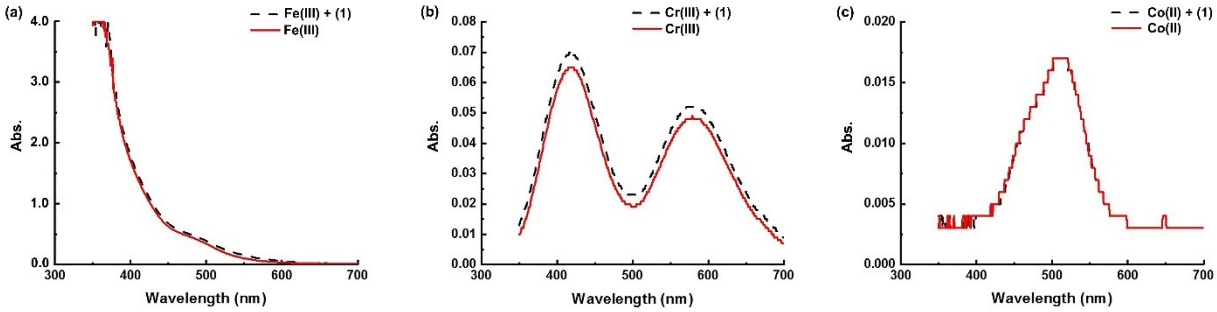


Fig. S8 Interfering visible-light absorption of (a) Fe(III) ions (30 μM) in water and Fe(II) with **1** (1 equiv.) in aqueous solution (ethanol:water = 50:50, v/v), (b) Cr(III) ions (30 μM)) in water and Fe(II) with **1** (1 equiv.) in aqueous solution (ethanol:water = 50:50, v/v), and (c) Co(II) ions (30 μM)) in water and Fe(II) with **1** (1 equiv.) in aqueous solution (ethanol:water = 50:50, v/v).

References.

(1) Z. Y. Xie, F. Heo, J. Su, Y. Yang, C. Yin, X. Yan and S. Jin, *Open Journal of Applied Biosensor*, 2012, **1**, 44-52.

(2) G. Han, D. Hong, B. S. Lee, E, Ha. J. H. Park, I. S. Choi, S. M. Kang, and J. K. Lee, *Chem. Asian J.* 2017, **12**, 846-852.

(3) A. M. Brouwer, *Pure Appl. Chem.,* 2011, **83**, 2213-228.