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A colorimetric, NIR, ultrafast fluorescent probe for ferric iron based on PET mechanism and its multiple application

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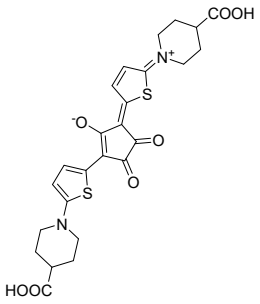
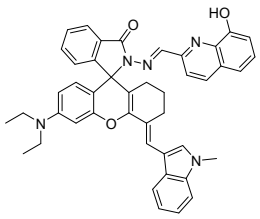
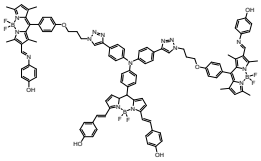
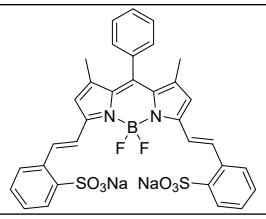
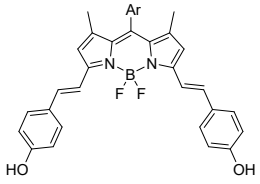
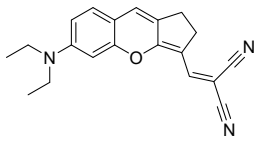
Table S1 NIR fluorescent probe recognition of Fe^{3+} published by literature

No.	Target	Molecular structure	$\lambda_{ex}/\lambda_{em}$ (nm)	LOD (μM)	Application	Literature
1	Fe^{3+}/ Cu^{2+}		—/818	—	none	Tetrahedron **2015**, 71, 5478
2	Fe^{3+}		650/700	0.12	Living cells Zebrafishes	J. Lumin. **2019**, 207, 613.
3	Hg^{2+} /Fe^{3+}		460/670	0.515/ 0.681	Living cells	J. Mater. Chem. B **2016**, 4, 7549.
4	Fe^{3+}		565/628	0.0142	Water sample	J. Photochem. Photobiol., A **2018**, 355, 78.
5	Fe^{3+}		378/697	3.75	Living cells	Spectrochim. Acta, Part A **2020**, 228, 117720.
6	Fe^{3+}		570/670	19.47	Living cells Lake water Tap water anti-counterfeiting ink	This work

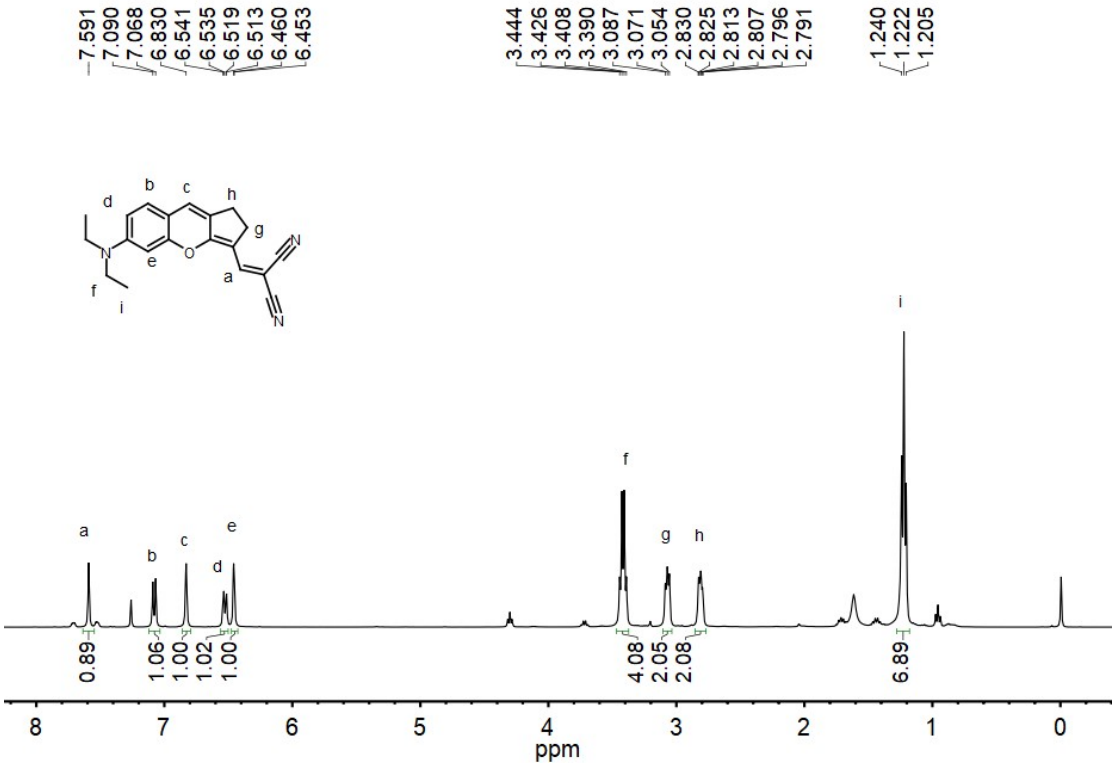


Figure S1. ^{1}H NMR spectrum of compound **DCA-Mln** in $CDCl_3$

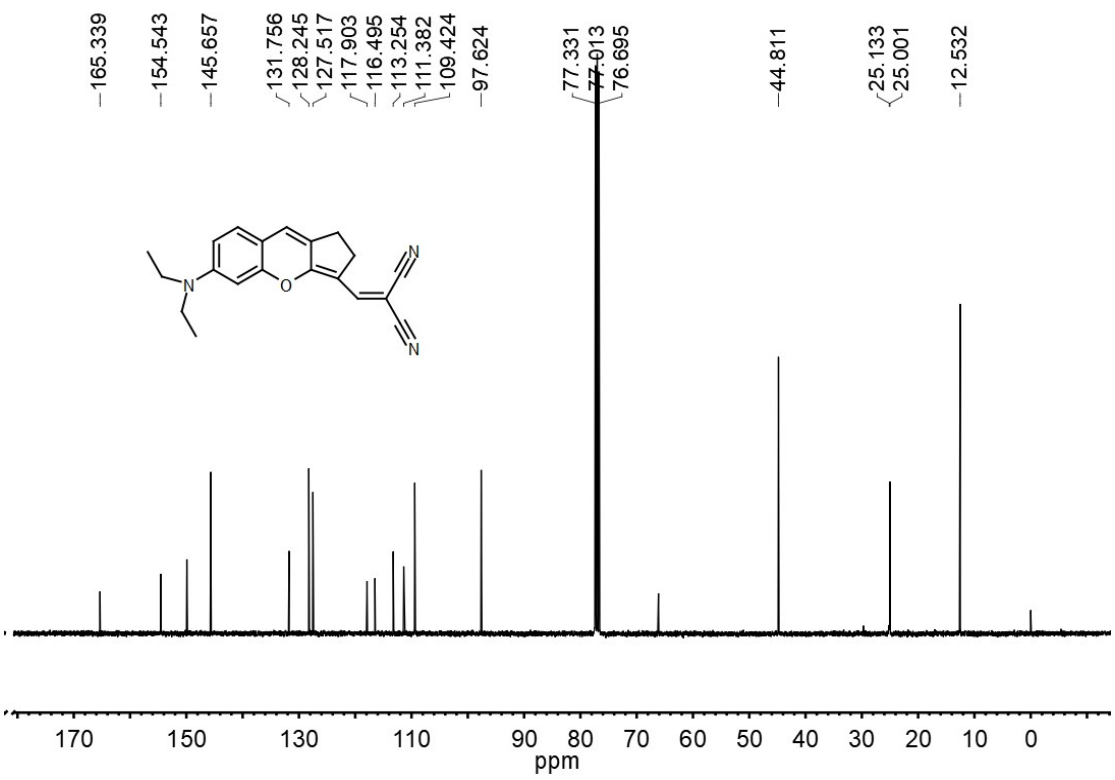


Figure S2. ^{13}C NMR spectrum of **DCA-Mln** in $CDCl_3$

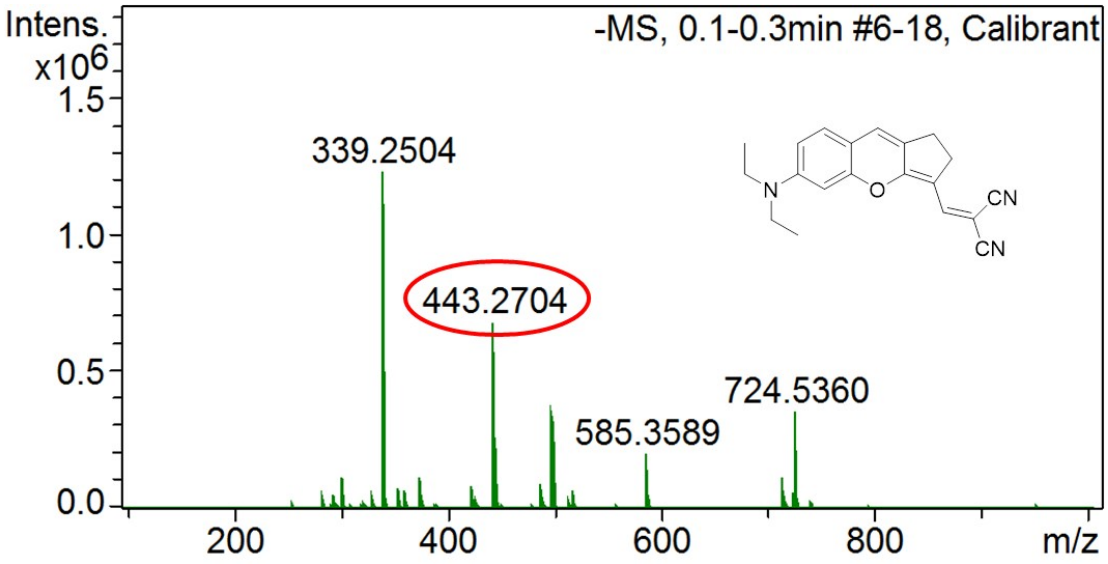


Figure S3. HRMS spectrum of **DCA-Mln** in CH_3CH_2OH

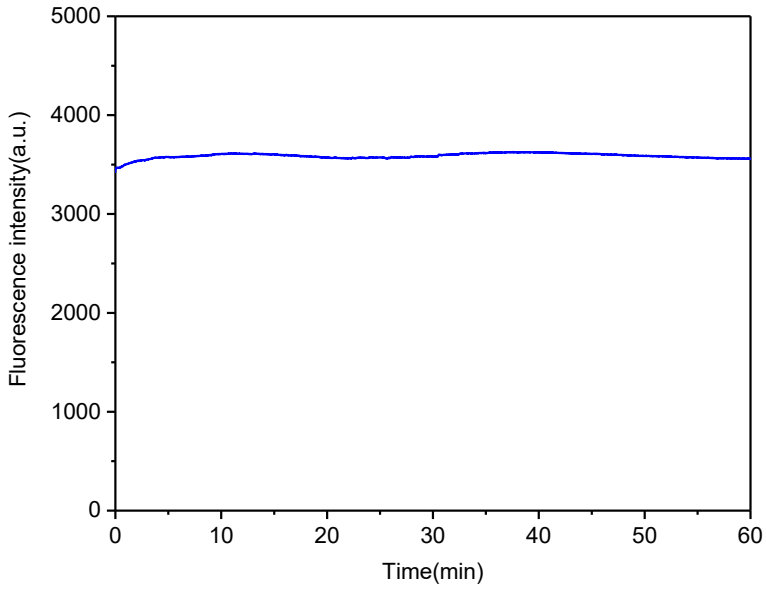


Figure S4. The change of fluorescence intensity of DCA-Mln over time

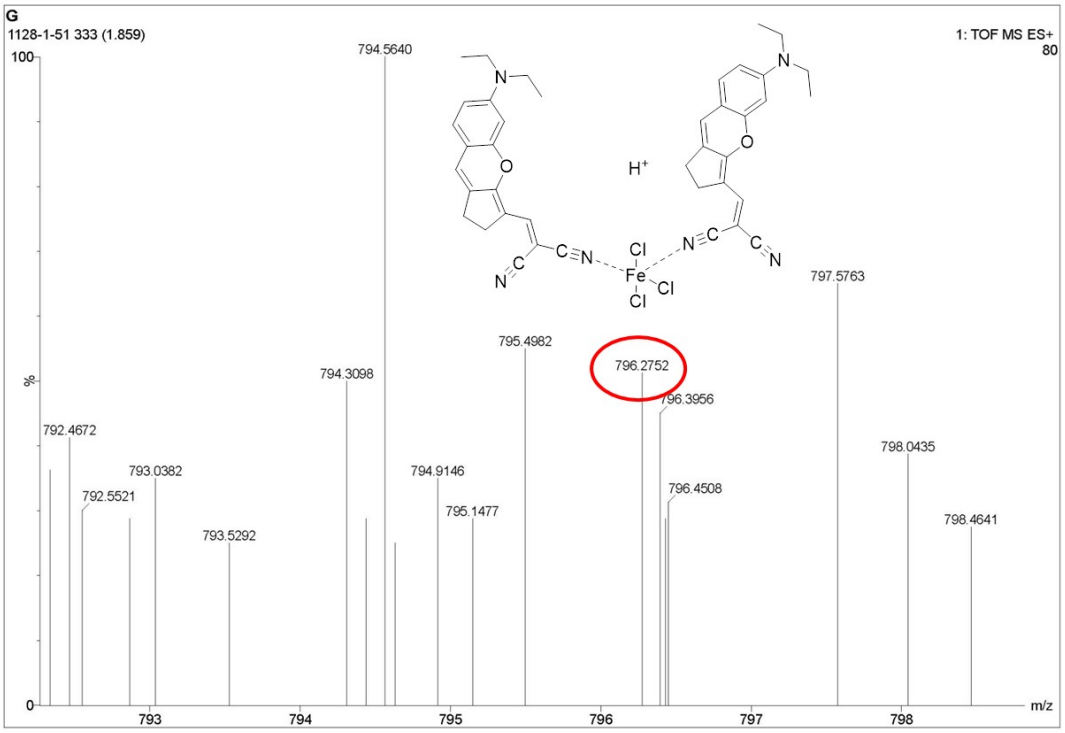


Figure S5. HRMS spectrum of compound **DCA-Mln** +Fe^{3+} in EtOH (ESI^{+}) calcd for $C_{40}H_{39}Cl_3FeN_6O_6^{+}$ $[2M+FeCl_3+H]^{+}$= 796.2544, Found=796.2752

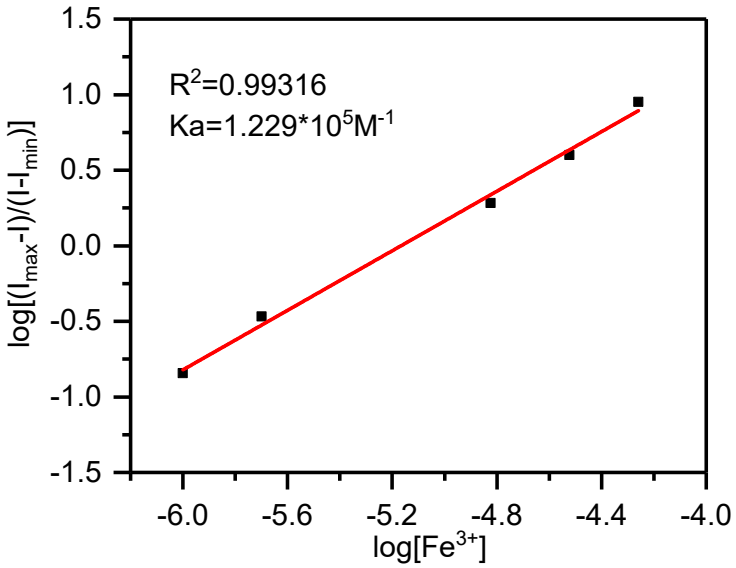


Figure S6. DCA-Mln and Fe^{3+} complex (2:1) combined with Hill equation diagram of stoichiometry

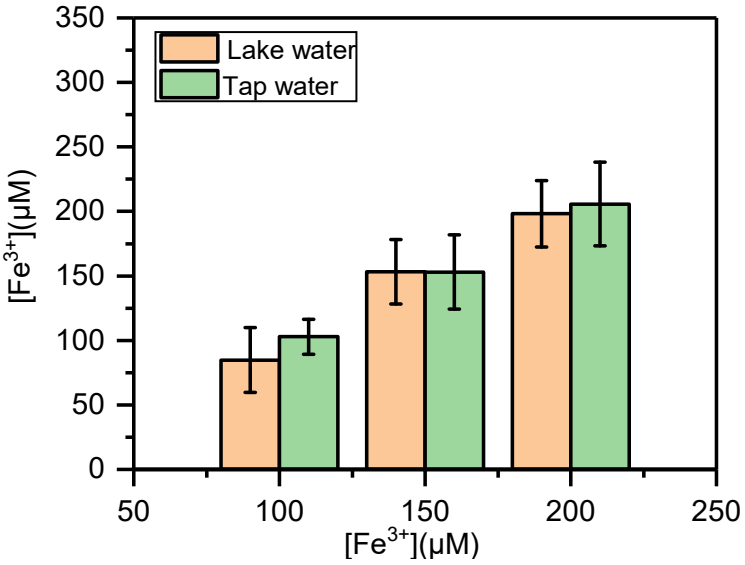


Figure S7. The concentration of Fe^{3+} using **DCA-Mln** (10 μM) detection in two actual water samples.

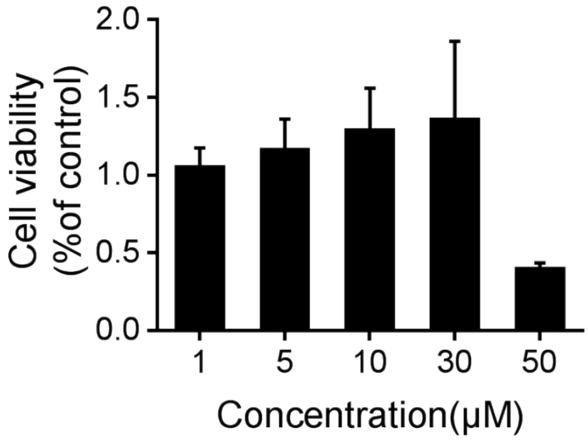


Figure S8. Cell viability evaluated by CCK-8 analysis after co-culturing MCF-7 Cells with different concentrations of **DCA-Mln** (1, 5, 10, 30, 50 μM) at 37 ^{o}C for 24 h.

Experimental

Instruments and materials

High-resolution mass spectra (HRMS) were measured using a Bruker micrOTOF-Q mass spectrometer (Bruker Daltonik, Bremen,Germany).^{1}H NMR and ^{13}C NMR spectra were recorded on an Agilent 400MR spectrometer, and the chemical shifts were expressed in ppm and coupling constants (J) in hertz. Use F-4700FL

Fluorescence Spectrophotometer (Japan) to measure the fluorescence spectrum. The pH measurement was carried out on a Model PHS-25 Bmeter (Shanghai, China). Cell imaging was observed under a confocal laser scanning microscope (LEICA TCS SP5 II, Germany) with excitation at 570 nm.

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. The compound **DCA** was prepared according to the reported method [S1]. MCF-7 (human breast carcinoma) cells were obtained from the Institute of Basic Medical Sciences (IBMS) of Chinese Academy of Medical Sciences (CAMS).

General methods of experiment

All experiments were carried out at room temperature. Deionized water was used throughout the experiment. A stock solution (50 mM) of cations (corresponding metal nitrate or chloride), $FeCl_3$ are used as iron ion sources. Prepare a stock solution of **DCA-Mln** at 10 mM in DMSO. It was further diluted with a mixed solution of MeOH/H_2O (v/v, 5/5) to a final concentration of 10 μM. The fluorescence spectrum was recorded by excitation at 570 nm. The width of the excitation and emission slits were both 5 nm.

Detection of Fe^{3+} in real water samples

We use the standard curve method for quantitative analysis. First, we tested the responses of the fluorescence emission intensity (670 nm) of **DCA-Mln** to various concentrations of Fe^{3+} in different water samples (lake water, tap water) using an excitation of 570 nm. Then, we obtained a linear relationship curve as the standard curve (Figure 9, y=kx+b, y:fluorescence emission intensity； x: concentration of Fe^{3+}). Finally, we used the standard additions method to determine the recovery. That means we added the different concentration of Fe^{3+} within the range of the standard curve, and tested the fluorescence intensity of **DCA-Mln**, and then x which is "Fe^{3+} found" value is calculated by substituting the fluorescence intensity value into the above-mentioned formula.

Cell viability assays

After the addition of different concentrations of **DCA-Mln** (10, 50, 100, 300, 500 μM), the incubated MCF-7 cells were cultured for 24 h. The 10 μL CCK-8 (Cell Counting Kit-8, Dojindo, Japan) was added into **DCA-Mln** -pretreated cells, and the cells were further incubated for another 4 hours. After being washed three times with PBS, the absorbance at 570 nm of cells was recorded, and cell viability was calculated using the reported methods of literature.

Preparation of anti-counterfeiting ink

DCA-Mln was dissolved using ethanol and a small amount of glycerin, after stirring 10 minutes to obtain anti-counterfeiting ink. The imprints of Chinese characters and English letters were obtained by using the stamp to dip anti-counterfeiting ink on the silicone plate, and then the imprints were observed using portable UV lamp.

Reference

[S1] Richard, Jean-Alexandre, Romieu, et al. Synthesis of N,N-dialkylamino-nor-dihydroxanthene-hemicyanine fused near-infrared fluorophores and their first water-soluble and/or bioconjugatable analogues. Chemistry An Asian Journal, 2017, 12(8):936-946.