

Supporting information

Probe Integrated with Laser-Induced Graphene Electrode: Application Towards multimodal Optoelectrochemical Detection of Cu(II) Ions and its Remediation.

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EXPERIMENTAL SECTION

1.1. General. All chemicals (solvents, reagents, and chemicals) were purchased from best-known local chemical suppliers and used without further purification. Solvents were distilled and dried prior to use. FTIR spectra were recorded on a Perkin-Elmer FT-IR Spectrum BX system and were reported in wave numbers (cm^{-1}). On the other hand, ^1H NMR and ^{13}C NMR spectra were recorded in a Bruker Avance Neo 400 spectrometer operating at 400 and 100 MHz for ^1H and ^{13}C NMR spectroscopy, respectively. Chemical shifts were reported in ppm downfield from the internal standard, tetramethylsilane (TMS). Mass spectra were recorded on Shimadzu LC-MS. Scanning electron microscopy (SEM) image was observed on a FEI Quanta 400 FEG instrument.

1.2. Spectroscopic studies. The UV-vis spectroscopic studies were recorded on a JASCO (model V-650) UV-Vis spectrophotometer. The slit-width for the experiment was kept at 5 nm. Sensing was carried out by adding requisite amounts of $\text{Cu}(\text{NO}_3)_2$ to CH_3CN solutions of probes (1×10^{-6} M). On the other hand, fluorescence experiments were performed in FluoroLog-TM (Horiba Scientific). The slit-width for the fluorescence experiment was kept at 5 nm (excitation) and 5 nm (emission) and the excitation wavelength was set to 280 nm.

1.3 Fluorescence Titrations: Stock solutions of 1 mM of FCN was prepared in DMSO. A standard fluorescence cuvette (10 mm) was filled with 2 mL of the respective solvent, to which 10 μL of probe FCN (10 μM) was added. An initial PL spectrum was recorded using $\lambda_{\text{ex}} = 280$ nm. Subsequently, increasing concentrations of $\text{Cu}(\text{NO}_3)_2$ were added to the probe solution and the PL was recorded.

1.4. Detection limit determination. The method used for the calculation of the detection limit is known as the blank variability method. In this method, the calibration curve was prepared by recording fluorescence spectra of 1 in different amounts of $\text{Cu}(\text{NO}_3)_2$.

From the equation obtained from the calibration plot, the added $\text{Cu}(\text{NO}_3)_2$ concentrations were calculated. Then another calibration curve was drawn between the C_{real} (added $\text{Cu}(\text{NO}_3)_2$, μM) vs. C_{calc} . (Calculated amount of $\text{Cu}(\text{NO}_3)_2$, μM). This afforded a value of the slope (b).

The fluorescence spectra of FCN were taken as blank reading. A total 10 replicates of the blank were measured. The standard deviation from the blank readings was calculated by fitting the fluorescence reading into the equation obtained from the first calibration curve (titration spectra). Using this standard deviation value, we calculated decision limit by this following equation.

$$L_C = t_c \times s \times (1 + 1/N)^{1/2} \dots \dots \dots (1)$$

where, N = the number of blank replicates taken; the value of t_c for 10 blank readings is 1.833; and s = the standard deviation value.

The detection limit (L_D) was calculated as the double of the decision limit obtained,

$$L_D = 2 L_c \dots\dots\dots (2)$$

In concentration term, the detection limit appeared as,

$$x_D = 2 \times C = 2 L_c / b \dots\dots\dots (3)$$

where, b = slope of the second calibration curve (C_{real} vs. C_{calc}).

1.5. ¹H NMR Studies. ¹H NMR titration studies of FCN were performed with Cu(NO₃)₂ (1.0 equiv.) in CDCl₃. The spectra were recorded using identical parameters.

SYNTHESIS AND CHARACTERIZATION

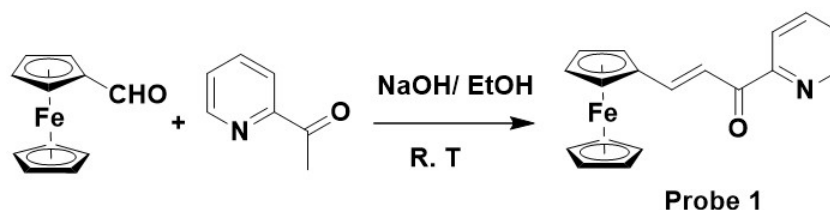
1.1 Synthesis of FCN/FCS/FCO

In a round bottom flask, a mixture of ferrocene carboxaldehyde (100mg, 0.467 mmol) and the corresponding 2-acetyl aryl (1 equiv.) and 3 M of aqueous sodium hydroxide (1 mL) in ethanol (2 mL) was stirred at room temperature for 3 hours. Then, the crude product was collected by filtration and dried, resulting in red powder. The formation of the product was confirmed by NMR. Yield: 90%.

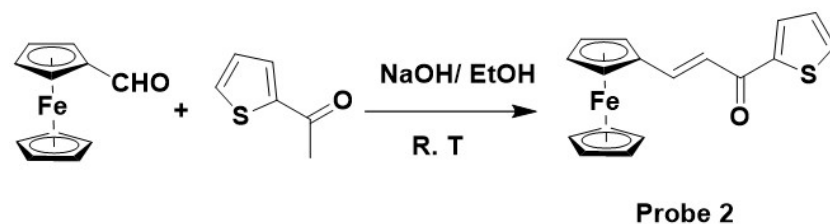
FCN: $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.73 (d, $J = 4.1$ Hz, 1H), 8.19 (d, $J = 7.7$ Hz, 1H), 7.85 (dd, $J = 16.8, 10.5$ Hz, 3H), 7.48 (dd, $J = 15.1, 10.2$ Hz, 1H), 4.68 (s, 2H), 4.50 (s, 2H), 4.18 (s, 5H).

FCS: $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.79 (d, $J = 15.6$ Hz, 2H), 7.65 (d, $J = 4.5$ Hz, 1H), 7.17 (d, $J = 4.6$ Hz, 2H), 7.02 (d, $J = 15.4$ Hz, 2H), 4.60 (s, 2H), 4.49 (s, 2H), 4.19 (s, 3H).

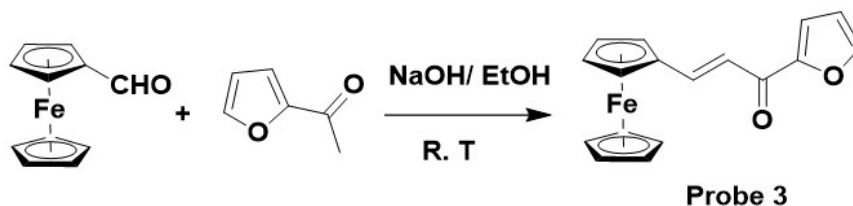
FCO: $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.82 (d, $J = 15.5$ Hz, 1H), 7.64 (s, 1H), 7.03 (t, $J = 12.7$ Hz, 1H), 6.58 (s, 1H), 4.61 (s, 2H), 4.49 (s, 2H), 4.18 (s, 5H).



Scheme. S1: Synthesis of FCN



Scheme. S2: Synthesis of FCS



Scheme. S3: Synthesis of FCO

ADDITIONAL SPECTROSCOPIC DATA

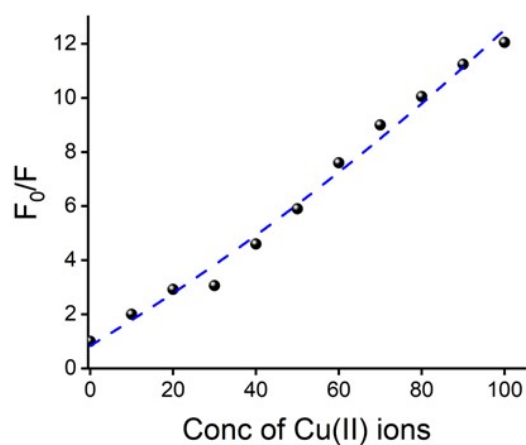


Figure. S1: Stern-Volmer plots (F_0/F) for the fluorescence quenching of FCN upon incremental addition of Cu(II) ions.

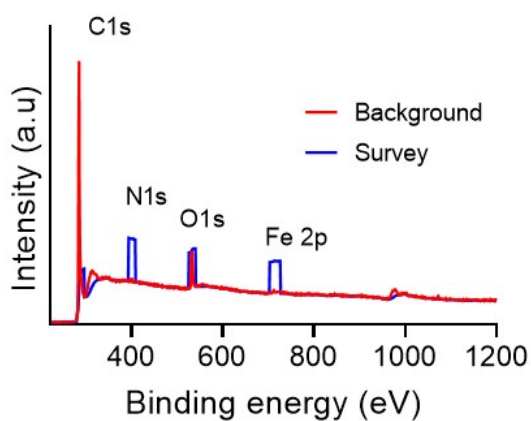


Figure. S2 XPS Survey spectra of FCN@LIG.

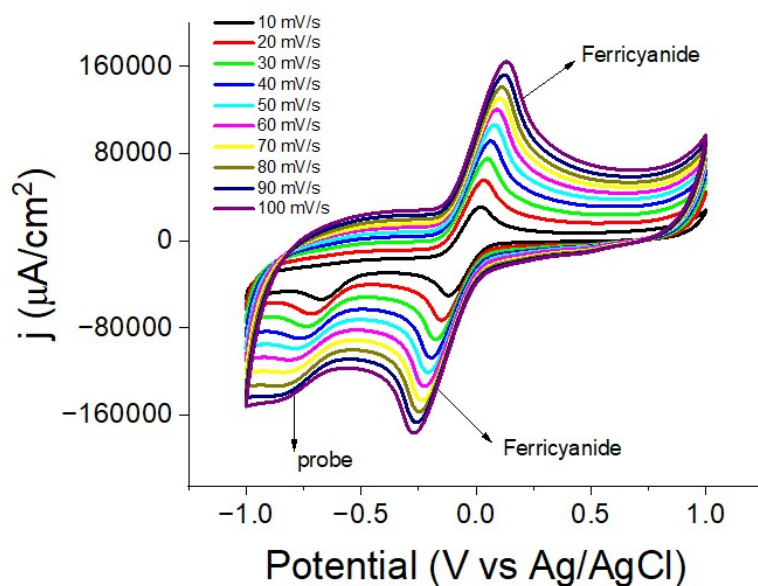


Figure. S3: Cyclic voltammogram of **FCN@LIG** with the potassium ferricyanide–KCl solution for 50 mV/s scan rate.

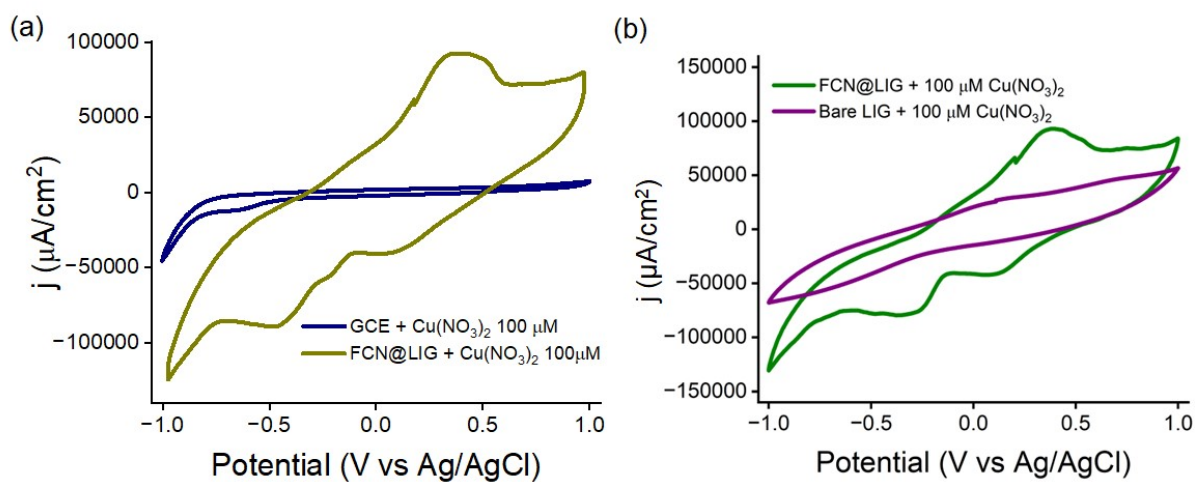


Figure. S4: Cyclic voltammogram of (a) GCE and **FCN@LIG** upon addition of 100 μM $\text{Cu}(\text{NO}_3)_2$ (scan rate: 50 mV/s). (b) Bare and **FCN@LIG** upon addition of 70 μM $\text{Cu}(\text{NO}_3)_2$ (scan rate: 50 mV/s).

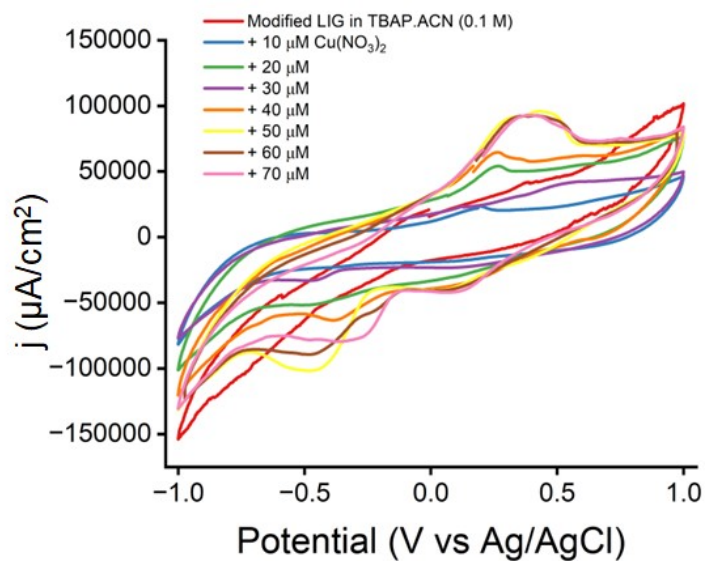


Figure. S5: Cyclic voltammogram of **FCN@LIG** upon addition of $\text{Cu}(\text{NO}_3)_2$ (0-100 μM) (scan rate: 50 mV/s).

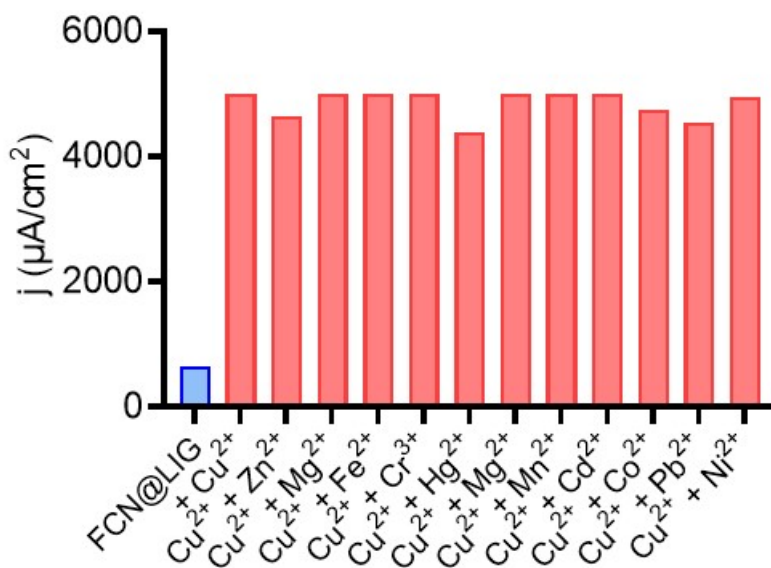


Figure. S6: Bar plot showing interference effect analysis of **FCN@LIG** with the $\text{Cu}(\text{II})$ ions and other potent interfering metal ions by chronoamperometry.

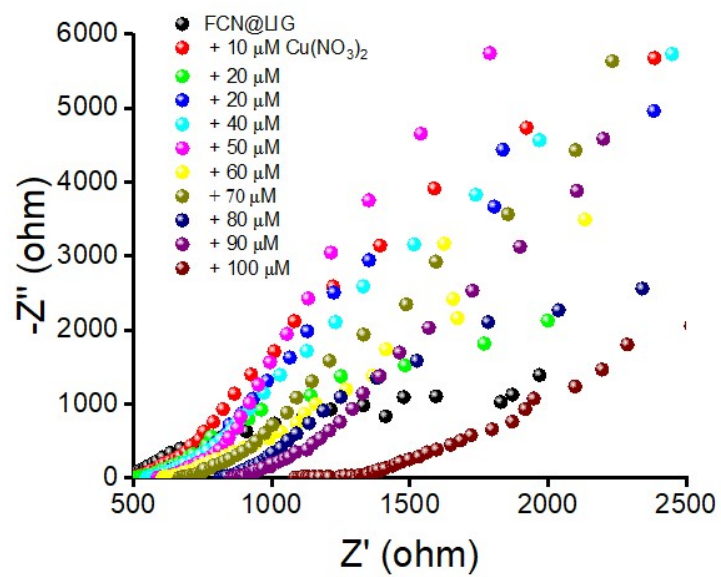


Figure. S7: Electrochemical Impedance spectroscopy (EIS) of probe FCN@LIG upon addition of Cu(II) ions (0-100 μM) in CH_3CN .