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Selective Iodide Chemosensing Through a Redox-active Cu-corrole

Supplementary Information

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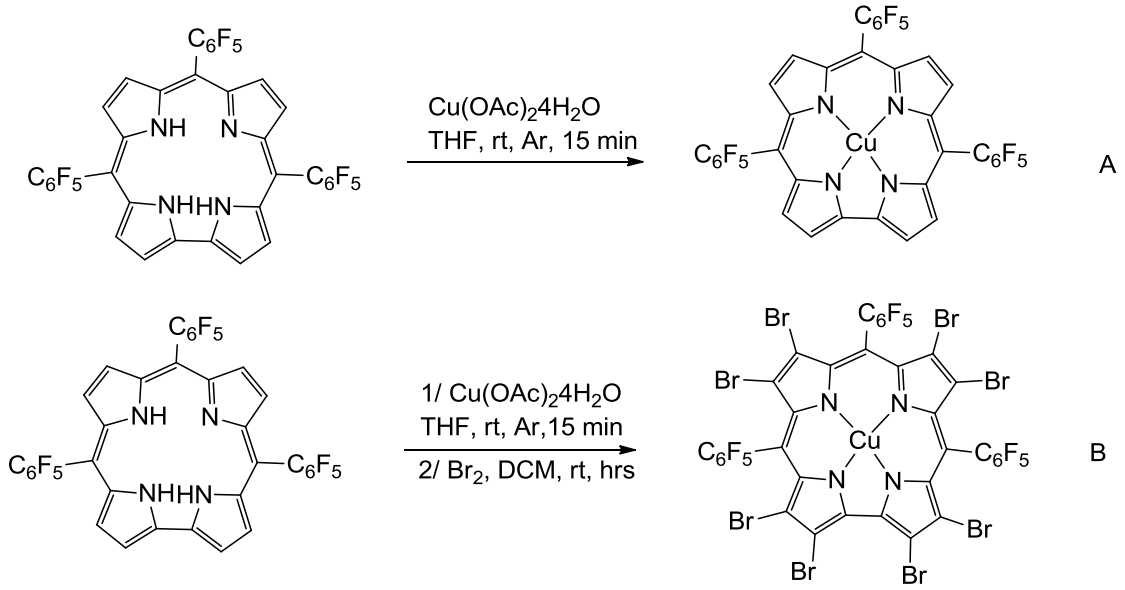
1. General Information (S1)

All solvents and reagents were purchased from commercial sources and used without further purification except for dry THF which was further distilled over sodium metal. Mass spectra were recorded on a Bruker LR-MS spectrometer using CH_3OH and $CHCl_3$ as solvent. 400 MHz for ^1H NMR and 376 MHz for ^{19}F, spectra were recorded using a Bruker instrument operating at 400 MHz in $CDCl_3$ with TMS as internal reference. EPR spectra were recorded using broker spectrometer in CH_2Cl_2. UV/Vis spectra were recorded on Shimadzu spectrophotometry UV-1800. Cyclic voltammograms were carried out using three-electrode system consisted of a Pt disk working electrode, a saturated calomel reference electrode (SCE) and a Pt-wire counter electrode. UV/Vis titration experiments were carried with stock solution of **B** (1 mM) and diluted for further analysis, prepared in HPLC grad DCM solvent. Experiments were carried under ambient conditions. All titration measurements were performed titrating receptor (B) with [n-Bu4N] $^+X^-$(X^- = F^-, Cl^-, Br^-, I^-, AcO^-, NO_3^-, SO_4^- and $H_2PO_4^-$) in DCM at 25 ºC.

2. Synthesis of compounds (S2)



Scheme 1. Preparation of compound **A** and **B**

Synthesis of copper(III)5,10,15-tris(pentafluorophenyl)corrole(A)[1] **:** The 5,10,15 tris(pentafluorophenyl)corrole (80mg, 0.1mmol) was dissolved in 30 ml of $CHCl_3$/MeOH(1:2) at room temperature and 120mg (0.8mmol) of $Cu(OAc)_2.4H_2O$ was added to it. The mixture was stirred for 30 minute. The solvent was removed at reduced pressure and the product was obtained by column chromatography of the residue on silica gel with CH_2Cl_2/hexane (2:1) as eluent. Yield = 80%; ^{1}H NMR (400MHz; CDCl3; Me_4Si,298K) 6.99 (2 H, br s, β-pyrrolic), 7.19 (2 H, br s, β- pyrrolic), 7.36(2 H, d, J 4.3, β- pyrrolic), 7.96 (2 H, br s, β- pyrrolic); ^{19}F NMR ($CDCl_3$, 376 MHz, 298K); 136.72 (dd, ^{1}J= 24.2, ^{2}J=6.2 Hz, 4F), 137.59 (dd, ^{1}J=137.59, ^{2}J=6.8 Hz, 2F), 151.90 (t, J=21.06 Hz, 2 F), 151.94 (t, J=20.84 Hz, 1 F), 160.53(m, 6 F); LR- MS (ESI): 855.96 (M^+); calcd 855.98.

Synthesis of Copper(III) ß-Octabromo-meso-tris(pentafluorophenyl)corrole(B)[2] **:** 5,10,15 tris(pentafluorophenyl)corrole (160mg,0.2mmol) and $Cu(OAc)_2 4H_2O$ (1.6 mmol) were dissolved in 60ml of $CHCl_3$/MeOH (1:2) and the mixture was stirred for 30 minute in room temperature. All solvents were evaporated at reduced pressure and the residue was diluted using 50ml $CHCl_3$ then filtered through anhydrous $NaSO_4$. The filtrate was taken and Br_2 (15mmol) dissolved in 15ml of $CHCl_3$ was added into the solution dropwise over a period of 10 minute. After 1.5 hrs, Pyridine (7.2mmol) was added dropwise over a period of 15 minute and the solution was further stirred for another 1.5 hrs. Mixture was washed with aqueous 20% w/v sodium metabisulfite solution. The organic layer was collected and dried over anhydrous $NaSO_4$. The solvent was evaporated at reduced pressure, purification by column chromatographic on a silica gel and $CHCl_3$/Hexane (1:1) as an eluent gave a brown red colored solid which was characterized. Yield = 60%; ^{19}F NMR ($CDCl_3$, 376 MHz, 298K); 137.75 (dd, 4F), 137.55 (dd, 2F), 149.30 (m, 3F), 161.07 (m, 6 F); LR- MS (ESI): 855.96 (M^+); calcd 855.98.1487.21 (M^+); calcd 1487.2565.

3. ^{1}H, ^{19}F NMR and Mass spectra (S3)

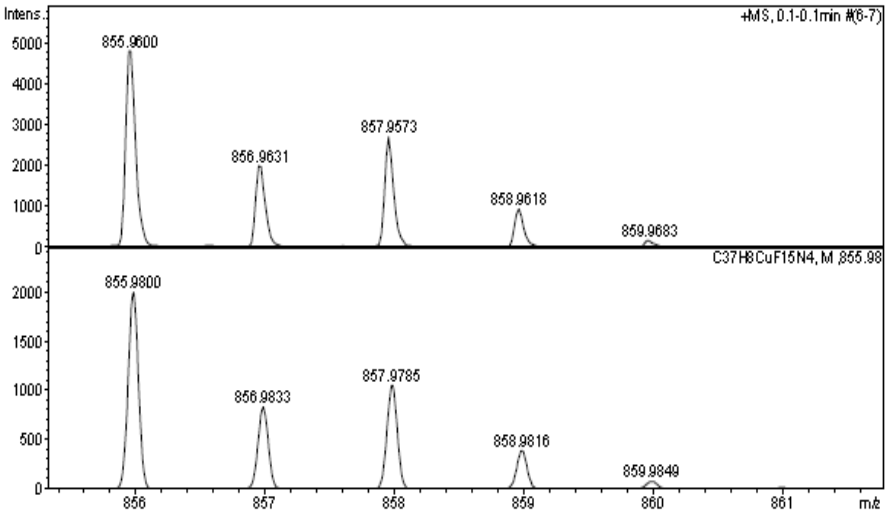


Figure 1. LR-GCMS of compound **A**

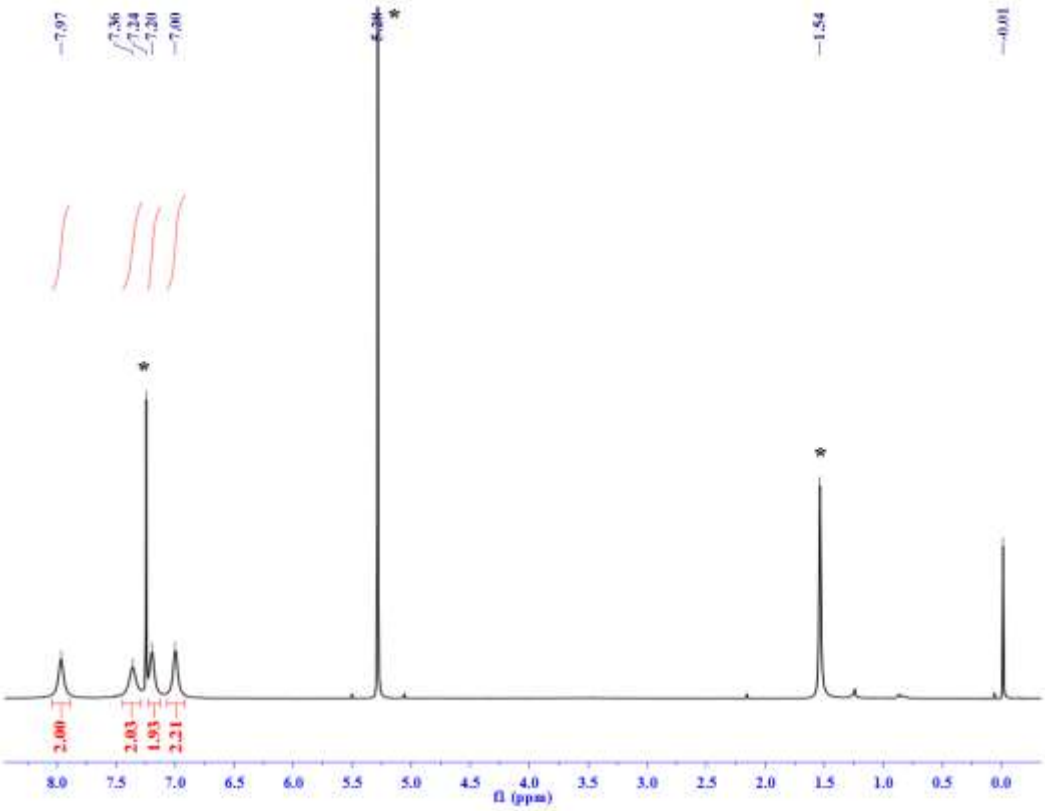


Figure 2. ^{1}H NMR of compound **A** $CDCl_3$ at 25°C

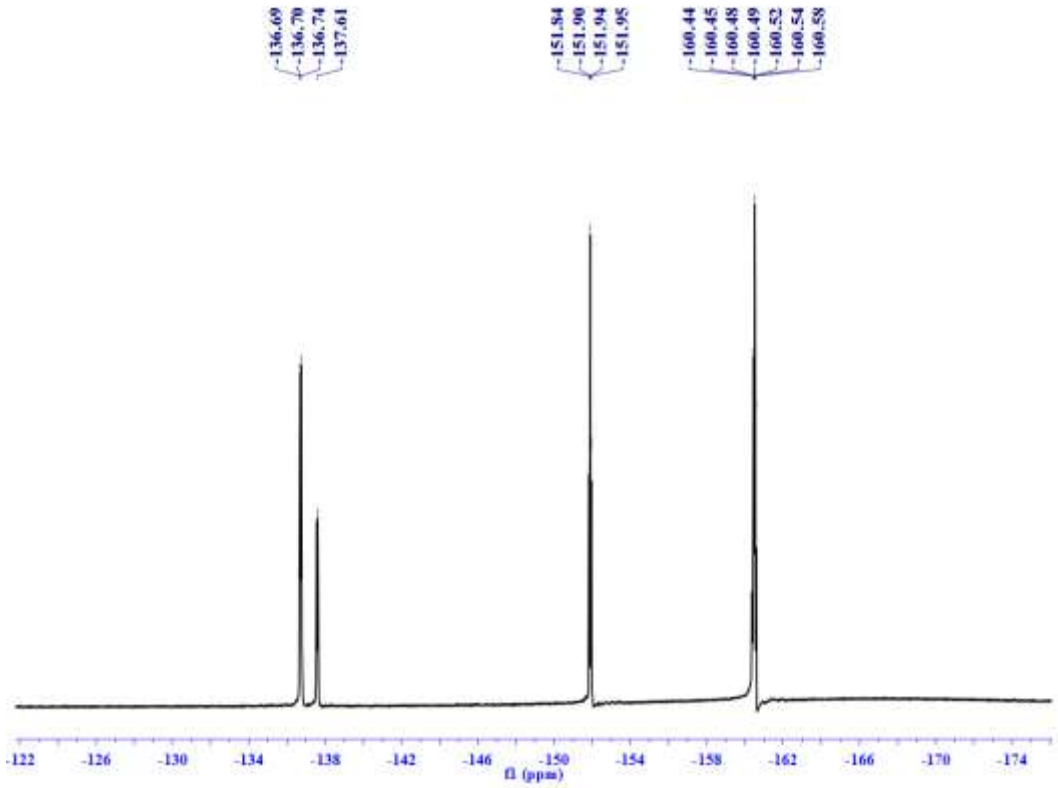


Figure 3. ^{19}F NMR of compound **A** in $CDCl_3$ at 25°C

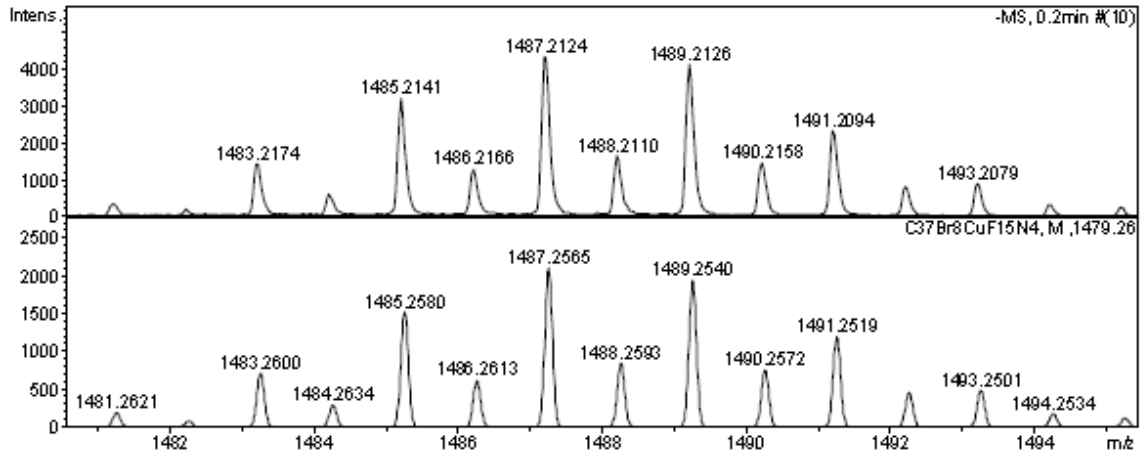


Figure 4. LR-GCMS of compound **B**

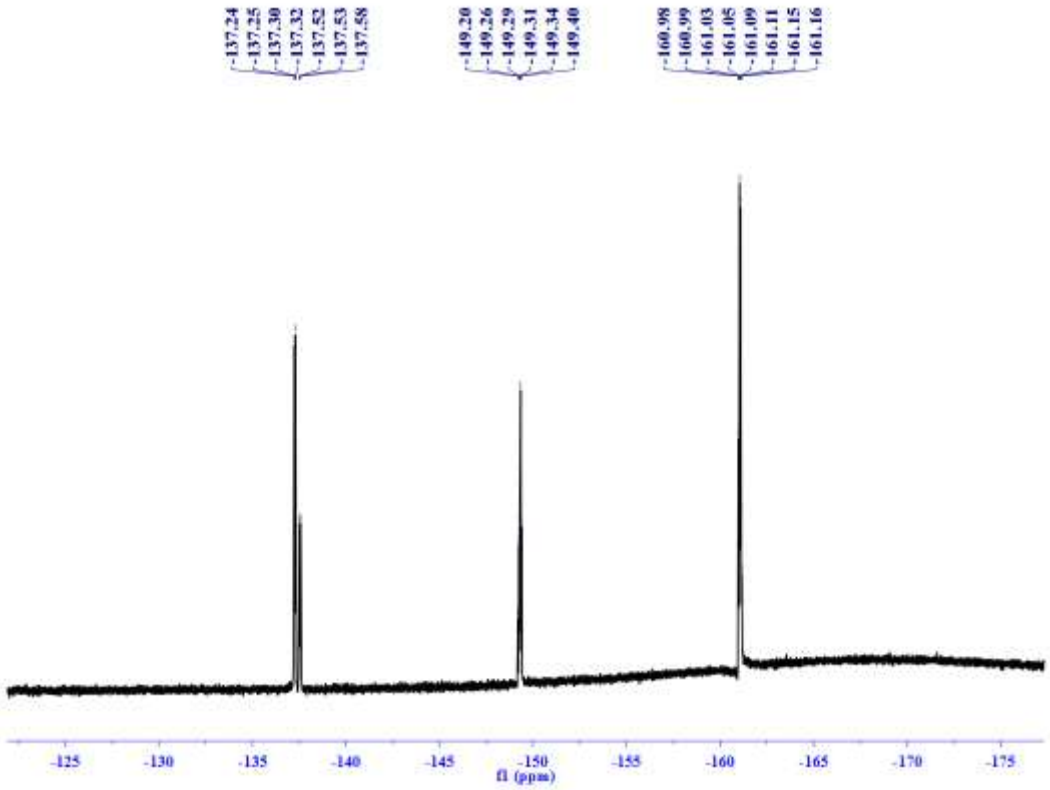


Figure 5. ^{19}F NMR of compound **B** in $CDCl_3$ at 25°C

4. Absorption titration spectra (S7)

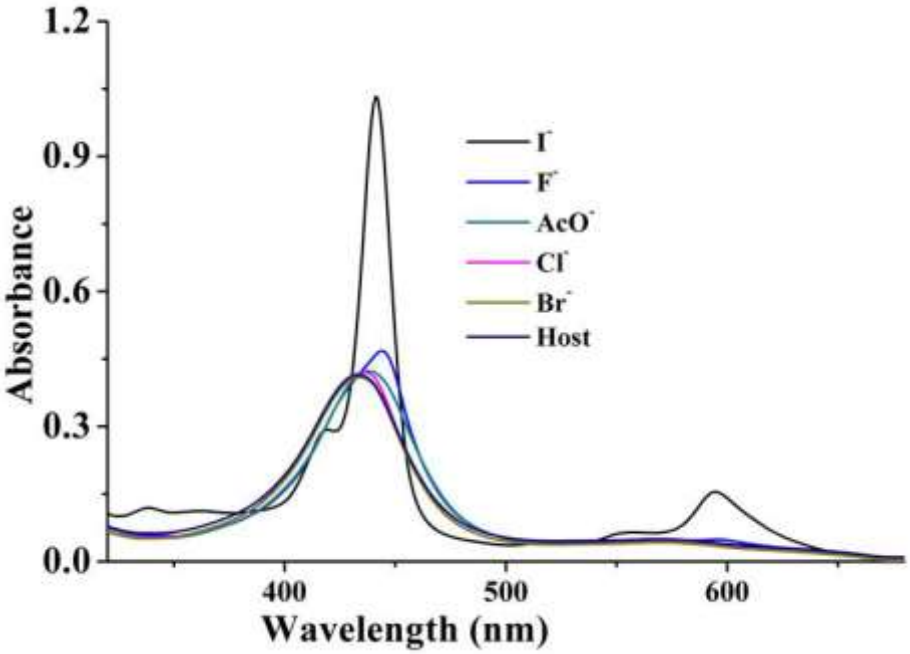


Figure 6. Changes in the absorption spectra of **B** (1.7μ M) with addition (4 equiv) of different anions in DCM.

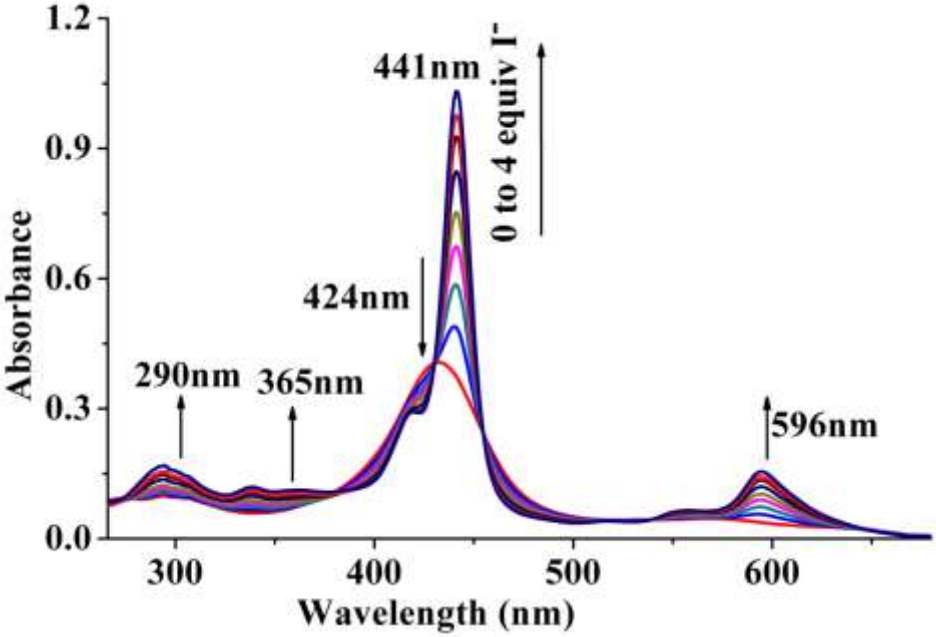


Figure 7. Changes in the absorption spectra of **B** (1.7μ M) with addition of various equivalents of I^- (0.6 mM) in DCM.

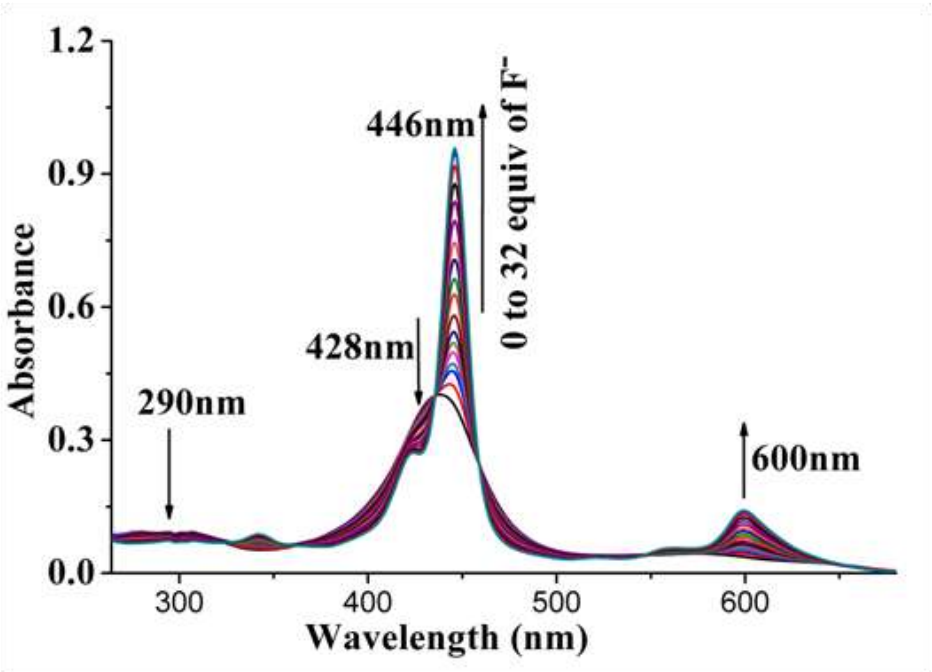


Figure 8. Changes in the absorption spectra of **B** (1.7μ M) with an increasing amount of F^- (0.6mM) in DCM.

5. Visual color changes of B with various anions (S8)

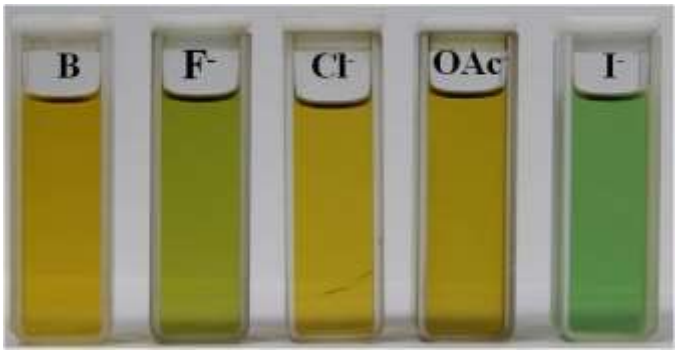


Figure 9. Color changes observed upon the addition of different anions (4 equiv. of 10mM) to **B** (1mM) in DCM.

6. Calibration curve for determination of iodide (S9)

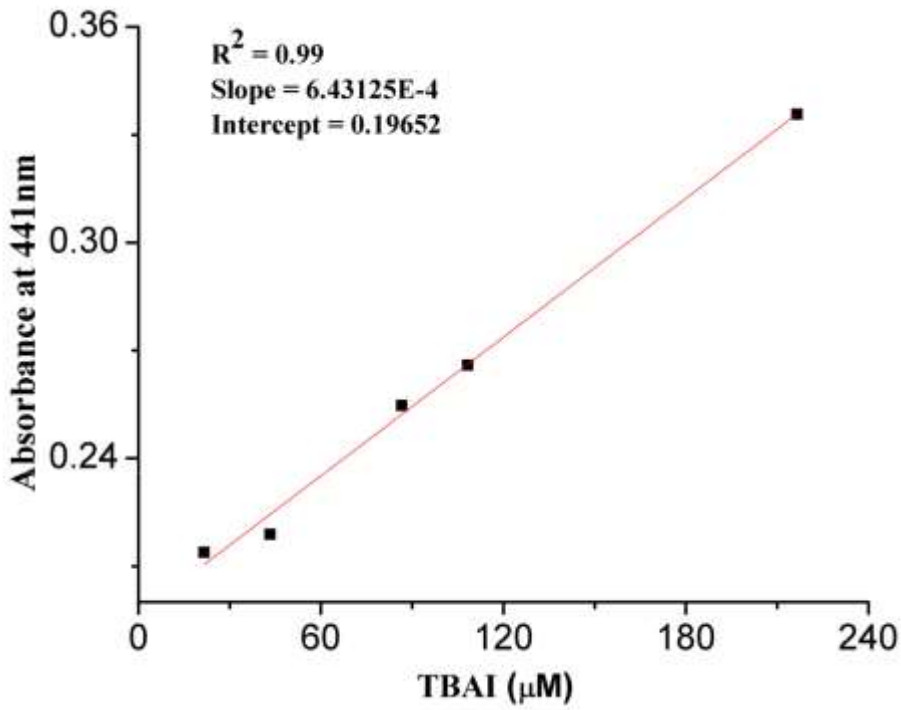


Figure 10: Calibration curve for detection of lowest detection limits.

With the help of this calibration curve, the Limit of detection (LOD) was calculated using below formula:

$$\text{LOD} = 3\sigma/s$$

Where 'σ' refers to standard deviation in the blank measurements and 's' indicates the slope of calibration curve.

7. Cyclic voltammograms (S10)

Cyclic voltammograms of **B** (CuIII/CuII), I^-/I_2 and Br^-/Br_2 redox coupled has been reported in DCM at 25°C, 0.1M TBAP was used as supporting electrolyte. Tetrabutyl ammonium iodide (TBAI) and Tetrabutyl ammonium bromide (TBABr) was used as I^- and Br^- sources respectively.

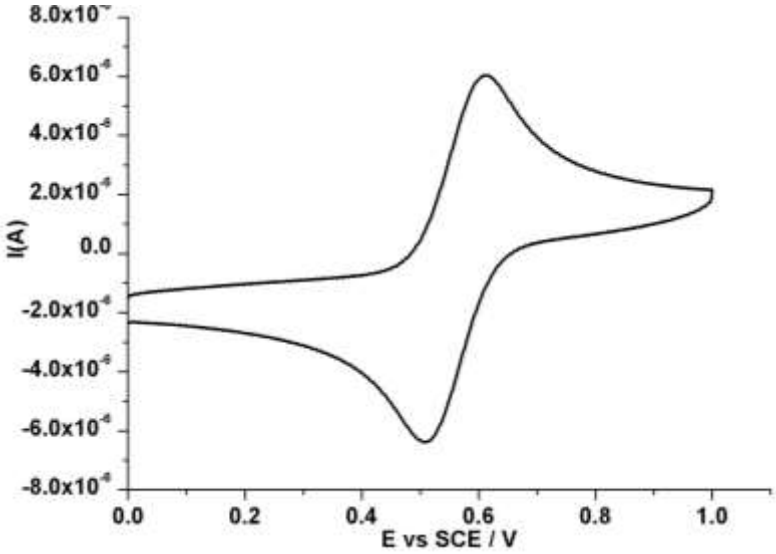


Fig11: Cyclic voltammogram of **B** at scan rate 0.1V/s

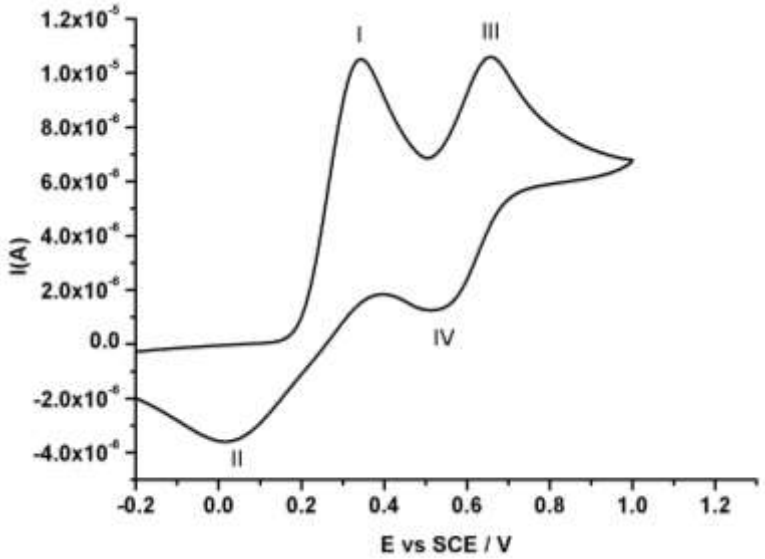


Fig12: Cyclic voltammogram of TBAI at Scan rate 0.2V/s

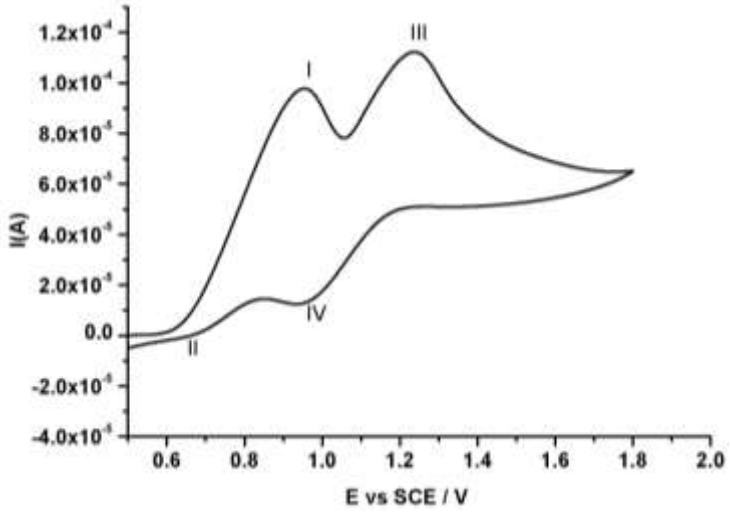


Fig13: Cyclic voltammogram of TBABr at Scan rate 0.2V/s

References:

1 (*a*) B. Koszarna and D. T. Gryko, *J. Org. Chem.* 2006, **71**, 3707; (*b*) I. Luobeznova, L. Simkhovich, I. Goldberg and Z. Gross, *Eur. J. Inorg. Chem.* 2004, 1724.
2 I. H. Wasbotten, T. Wondimagegn and A. Ghosh, *J. Am. Chem. Soc*., 2002, **124**, 8104.