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Selective Iodide Chemosensing Through a Redox-active Cu-corrole

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An electron deficient Cu(III)-corrole (B) has been identified as highly selective colorimetric sensor for iodide. A one-electron redox couple between iodide and Cu(III)-corrole serves as the basis for selectivity. The proposed mechanism has been supported by UV-Vis and ^{19}F NMR studies and further by unambiguous identification of Cu(II) species through EPR.

Exploration and design of new functional materials with novel applications in the field of anion recognition has attracted considerable attention over the past few decades.[1] This is certainly owing to the decisive role of anions in myriad of processes involved in biology, chemistry, industry and environment.[2]

Among various anions, iodide subsists as an indispensable entity due to its key role in various physiological activities such as brain function and cell metabolism. It is also an essential micronutrient for normal human growth and plays vital role in proper functioning of thyroid.[3] According to world health organization (WHO), deficiency of iodide exist as a major cause for mental retardation. Further, iodine is an essential element in sea water in the form of iodide and iodate species. In addition to this, environmental iodine is used for synthesizing many organic chemicals, manufacture of certain dyes and medicine.[4]

Owing to its fundamental roles in day-to-day life and crucial physiological relevance, various methods in the form of gas chromatography[5a] atomic absorption spectrometry,[5b] capillary electrophoresis[5c], chemiluminescence,[5d] polarography,[5e] voltametry,[5f] ion-selective electrodes[5g-i] and electrostatic ion chromatography [5j] are proposed and in operation for iodide/iodine analysis. However, most of these techniques are time consuming and require sophisticated

instrumentation, demand expertise requirements along with complicated sample preparation protocols. On the other hand, colorimetric detection through molecular scaffolds has been proposed as a powerful alternative for fast and in-situ detection due to the sensitivity and simplicity of the approach. However, designing a chemosensor for selective recognition of iodide is challenging task owing to its low charge density, large ionic radius and weak hydrogen bonding abilities.[6]

To date, most of the chemosensor approaches for selective iodide sensing are mainly dominated by fluorescence quenching response due to heavy atom effect of iodide and size selective discrimination of iodide among other anions. These fabrications are based upon amide/urea, bis-imidazolium and benzimidazole derivatives, quantum-dot-based probes and conjugated polymers.[7] Very rare reports exist wherein, iodide recognition has been achieved through visual-colorimetric means.[8]

Scheme 1. Synthesis of Chemosensor **B**

With immense interest and motivation from our previous work regarding new anion-sensing approach for fluoride,[9] we attempted another strategy for selective halide sensing based upon electron deficient and redox-active Cu(III)-corrole. Owing to a direct pyrrole–pyrrole linkage in corroles, unique spectral properties along with ability to stabilize higher oxidation states of metals[10a],

they act as materials of choice for perceiving ion sensing through molecular tools.[10b-d] Further, an interesting metal center reduction observed in Cu(III)-corrole by Kadish and coworkers[11] through electrochemical means, followed by Gross *et al.*[12] with $Na_2S_2O_4$, prompted us to exploit the electron deficient Cu (III) centre in ß-octabromo-*meso*-tris(pentafluorophenyl)corrole (**B**) for anion recognition properties. We could achieve a highly selective iodide sensing through colorimetric signals visible to naked-eyes. To the best of our knowledge this presents a lone example wherein selective iodide recognition has been achieved through a one-electron redox couple between iodide and Cu(III)-corrole.

The corrole **B** was obtained in a two-step process. 5,10,15-tris(pentafluorophenyl)corrole (**A**) obtained through a reported procedure,[13a-b] was metallated with copper(II) acetate hydrate under reflux conditions, which on subsequent bromination provides **B.**[11c] The compounds were characterized by ^{19}F NMR, LRMS-ESI and UV-Vis spectroscopy (S1-S5).

Compound **A** shows a split Soret band at 407nm and broad Q-type band in 520-650nm, whereas **B** displays a single Soret band at 438nm and broad Q-type band shifted to 560-700nm in dichloromethane (DCM). Split Soret band in **A** occurs due to the reduced symmetry in the presence of three sterically crowded inner NH protons. [14] Metallation of **B** with Cu (III) induces planarity and in turn a single intense Soret band. Red shifted (30nm) Soret band in case of **B** is attributed to a strong electronic pull of eight peripheral beta–pyrrolic bromine atoms.

To test the ability of **B** towards anion sensing, experiment preceded with addition of selective anions such as F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^-, CH_3COO^- and PO_4^{2-} in the form of tetra butyl ammonium (TBA) salts in dichloromethane (DCM). Among which, only I^- produced a drastic colorimetric change. This was further monitored through absorption spectroscopy. Here addition of 0–4 equivalents of I^- resulted in significant changes of absorption band at 424nm, while rest of the anions interacted weakly, even with ten-fold additions to that of iodide (Fig. 1 and 2).
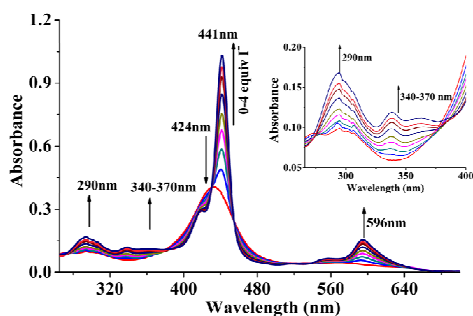
marked from yellow-brown to green (Fig. 5) color of the solution. Notably, in the case of F^-, a further 5nm red shift was observed in higher concentrations (Fig. 8 in SI), while other anions remained silent with respect to any notable shift or change in absorption profile even at higher concentrations. The changes are probably an outcome of electrostatic interaction of F^- with copper centre. Importantly, addition of iodide to **B** induced a noticeable difference *via* an increase in the intensity of absorption around 290nm and 360nm (Inset Fig. 1) region, whereas with F^-, a decrease in the intensity was observed (Fig. 8 in SI). With the help of calibration curve, detection limit of 7μM was calculated for iodide (Figure 10 in SI).
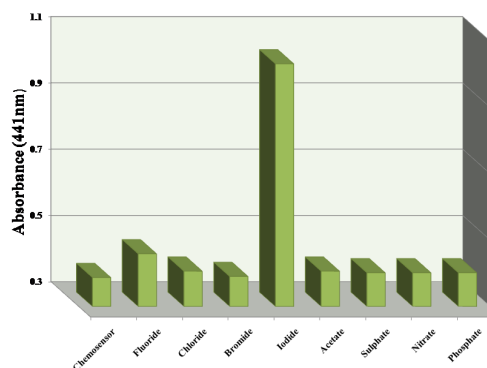

Fig 2. Bar graph presenting high selectivity of **B** for iodide in presence of various common anions in DCM. Observations were made with (1.7 μM) of **B** upon addition of 4 equivalents of I^- (0.6mM) and 32 equivalents of F^- (0.6mM) up to saturation level. Rest of the anions have been added up to 10-fold concentrations with respect to iodide.

In order to unravel the interaction, ^{19}F NMR titration of **B** in $CDCl_3$ was carried out with TBAI in DCM. Addition of iodide to **B** shows an initial broadening of fluorine peaks along with slight upfield shifted *para*-F and *meta*-F peaks (Fig. 3). Later attributes to the formation of a paramagnetic species in the system. The absence of a characteristic absorption at very short UV and long wavelength region ruled out any possible paramagnetic contribution from Cu (II)-corrole π-cation radical.[15]
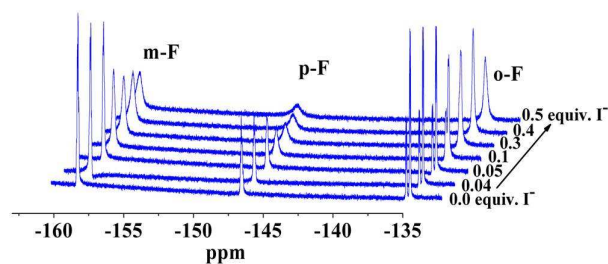

Fig 1. Changes in the absorption spectra of compound **B** (1.7μM) upon addition of 0-4 equivalents of Iodide in DCM. Inset showing the changes in short wavelength region of **B** with as a result of iodine.

An initial red shift of 424nm to 441nm was observed followed by a continual enhancement in the intensity upon further additions, while enhancement of 596nm was directly observed as a function of anion concentrations. The given changes were visibly

Fig 3: ^{19}F NMR spectral changes of **B** (1.2mM) in $CDCl_3$ upon addition of various equivalents of TBAI in DCM at 25°C. Ortho, meta and para fluoride peaks are assigned.

To understand the existence of paramagnetic species and explore the given mechanism of interaction, EPR experiments were carried out. Spectra of **B** (Fig. 4) in presence of excess iodide at 120K, indicates the formation of Cu(II)-corrole anion. The signal is centered at *g* = 2.035 and with four hyperfine

splitting due to ^{63}Cu (a_{cu} = 230G). The nine superhyperfine splitting due to four ^{14}N atom of reduced Cu(II)-corrole anion was observed, with a_N = 17G. The given observations were quite similar with that observed by Kadish and coworkers[11] by electrochemical reduction for [OEC(Cu)],⁻ where g = 2.092G and a_{cu} = 227G. The current observations match with the measurements reported by Gross *et al.*[12] Here, chemical reduction by sodium hydrosulfite results in the existence of [Cu(tdcc)]⁻ species with g = 2.033 and a_{cu} = 207.12G.
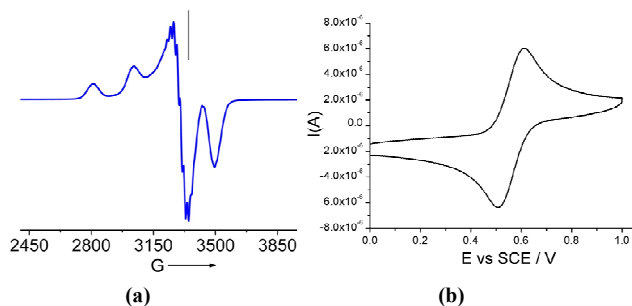

Fig 4: (a) EPR spectra of **B** in DCM at 120K with addition of iodide (10eqv). Instrument setting: Modulation frequency 100 KHz, Modulation amplitude 19 G and Center field 3400G. (b) Cyclic voltammogram of **B** in DCM at 25°C, 0.1M TBAP as supporting electrolyte, Scan rate = 0.1V/s

Hence the given peculiar selectivity of **B** correlates to one-electron oxidation of iodide by highly electron deficient Cu(III) centre (Fig. 5), *via* a strong electron-withdrawing trigger facilitated by bromine atoms. Enhanced absorbance band at 290nm and 350-370nm in **B** (Fig. 1 inset) in presence of I⁻ indicates formation of I₂ in the solution under consideration.[16] Importantly, the given color change is irreversible in nature even with addition to excess equivalent of water, which exclude possibilities of any weak electrostatic interaction.

Further, cyclic voltammogram (CV) of **B** shows first metal centre reduction from Cu(III) to Cu(II) at half wave potential, $E_{1/2}$ = 0.57V (Fig 4b).[11,17] To further ascertain our experimentally observed selectivity towards iodide, CV was conducted for I⁻ and Br⁻ under the same set of experimental conditions. An anodic oxidation peak at $E_{1/2}$ = 0.2V and a quasi reversible peak at half wave potential, $E_{1/2}$ = 0.58V was observed for I⁻ (SI Fig. 12). This attributes to two step oxidation processes in I⁻/I₂ redox couple.[18] Similar two step oxidation process was also observed in the case of Br⁻/Br₂ at 0.95V and 1.25 V (SI Fig. 13).[19] Redox potential values of Cu (III)/Cu (II) is sufficient to oxidize iodide to iodine, but is less positive than bromide / bromine couple.
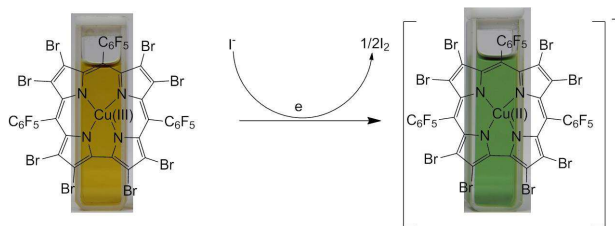

Fig 5: Proposed Mechanism of Iodide interaction and visible colorimetric changes.

In summary, we have presented a new and promising approach for selective sensing of iodide anion. A typical Cu(III)-corrole based molecular scaffold possessing a strong electron-withdrawing environment of bromine atoms around Cu-core seems a probable basis for the given selectivity. This triggers the single-electron redox couple in the medium under investigation. We hope the proposed strategy expose new doors in chemosensor designs for discrimination of iodide and other anionic species by fine tuning of its redox potential.

Notes and references

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