

Bis(*N*-methylindolyl)methane-based chemical probes for Hg²⁺ and Cu²⁺ and molecular IMPLICATION gate operating in fluorescence mode†Paramjit Kaur,*^a Sandeep Kaur^{a,b} and Kamaljit Singh*^b

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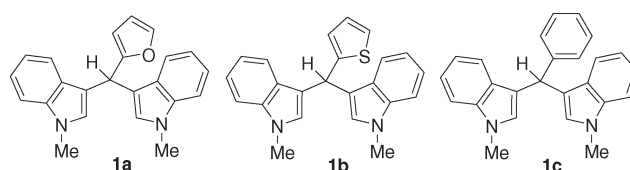
Bis(*N*-methylindolyl)methane derivatives behave as chemosensors for Hg²⁺ and Cu²⁺ ions relying on the absorption as well as emission changes. Rarely reported IMPLICATION logic gate operating in the fluorescence mode has been developed with respect to the emission band of one of the derivatives as output, with Hg²⁺ and I[−] as inputs.

Indole-based receptors have attracted considerable recent attention attributed to the acidity of the pyrrole NH group enhancing their binding affinity for anions. While Ghosh *et al.*¹ have reported the importance of indole-NH in detecting fluoride, Shao *et al.*² have demonstrated that introduction of the electron donating group into the indole-based skeleton can lower anion affinity of such systems with consequent augmentation of affinity towards cations. The cation-binding efficiency may depend upon the electron-donating power of the coordinating nitrogen atoms or the availability of the π -electron density for complexation.³ Modulating the electron donation of indole nitrogens by way of appending alkyl groups, we have demonstrated the feasibility of Hg²⁺ and Cu²⁺ recognition. Molina *et al.*⁴ have demonstrated the chemosensing behavior of *meso*-arylbis(indolyl)methanes for the Cu²⁺. We envisaged that in addition to the replacement of N–H function with the N–Me, the introduction of heterocyclic/aryl substituents at *meso*-position could modulate their sensitivity towards cations and may even lead to, yet less explored, multication sensing. In continuation of our research interest,⁵ we have explored chemosensing properties of the *meso*-substituted bis(*N*-methylindolyl)methane derivatives (**1a–c**) (Scheme 1 and S2, S3 in ESI†).

In line with our expectations, these systems are highly sensitive to the presence of heavy metal ions, Hg²⁺ and Cu²⁺. Detection of these two metal ions is important from the viewpoints of their environmental and biological relevance.

Considerable strides have recently been made⁶ to design and synthesize the sensor systems which present instantaneous optical response to these metal ions. Among heavy metal ions, mercury is an extremely toxic and environmentally hazardous⁷ element especially when present in the form of organic mercury such as methylmercury, which can lead to neurological, immunological, reproductive and cardiac disorders when absorbed by the human gastrointestinal tract.⁸ Inorganic mercury also is quite dangerous to the immune system and is neurotoxic.⁹ It produces a serious health concern when it accumulates in the food chain through air, water, vaccines, cosmetic products, *etc.*¹⁰ Cu²⁺, being third in abundance preceded by Fe²⁺ and Zn²⁺, plays a pivotal role in a variety of physiological processes¹¹ but can often be toxic to certain biological systems when its amount exceeds the cellular needs.¹² It is also implicated in Alzheimer's disease, prion diseases, Menkes and Wilson diseases, lipid metabolism and inflammatory disorders.¹³ Copper has been extensively used for the industrial, pharmaceutical and agricultural purposes¹⁴ due to its properties like chemical stability, high electrical conductivity, germicidal efficacy and ability to form alloys with other metal ions. But at the same time, its widespread use poses a serious threat to environment, which is attributed to its ionic form Cu²⁺.¹⁵ Therefore, the design and development of potential chemosensors for heavy metal ions is very important.

On the other hand, since the report of the first AND logic gate by de Silva *et al.*,¹⁶ a variety of molecular logic gates such as NAND, OR, NOR, XOR, INHIBIT, *etc.*¹⁷ have been reported and consequently molecular logic gates and their integrated operations have become one of the important focus of chemistry. However, with respect to the IMPLICATION gate, in which either input A implies the other input B or input B implies the other input A and are equal to the IF-THEN operation and the NOT operation (here NOT implies two inputs), there are very limited reports.¹⁸ In earlier reports, cation/cation^{18a} and cation/chelating agent (EDTA)^{18b} have been employed as two inputs.

Scheme 1 Structures of **1a–c**.

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Here, we wish to present one IMPLICATION gate operating in fluorescence mode with cation/anion, *i.e.* Hg^{2+} and I^- as two chemical inputs.

The UV-vis absorption spectra of **1a–c** (3×10^{-5} M, in CH_3CN) are characterized by a very strong band at 227 nm (**1a** and **1c** with ϵ_{max} 68 753 and 56 410 $\text{l mol}^{-1} \text{cm}^{-1}$, respectively), 228 nm (**1b** with ϵ_{max} 65 713 $\text{l mol}^{-1} \text{cm}^{-1}$) and a weak band at 291 nm (**1a** and **1b** with ϵ_{max} 10 796 and 11 103 $\text{l mol}^{-1} \text{cm}^{-1}$, respectively), 292 nm (**1c** with ϵ_{max} 9573 $\text{l mol}^{-1} \text{cm}^{-1}$). The emission spectra of **1a–c** are characterized by one strong emission band at 500 nm which is in contrast to the weak emissions reported for the *meso*-substituted bis(indolyl)methane.⁴ We attribute the strong emission to the photoinduced electron transfer (PET) process involving nitrogen lone pairs of the electrons, which is facilitated by the methyl substituted indole nitrogen. Before investigating the cation sensing properties of **1a–c**, the effect of pH variation was noted during titration of **1a–c** (3×10^{-5} M, in CH_3CN) with both HCl as well as NaHCO_3 (0.01 M). No significant change was observed in the respective absorption spectra over the covered pH range (2.0–12.0) (S4–S6, ESI[†]), thus demonstrating an advantage for rapid monitoring of analytes in environmental and biological settings without resorting to buffered media. Our preliminary investigations reveal that the absorption properties of **1a** and **1b** (3×10^{-5} M, in CH_3CN) are perturbed by both Hg^{2+} (added as perchlorate salt) and Cu^{2+} (added as nitrate salt) whereas that of **1c** only by Cu^{2+} over other metal ions, Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} (added as perchlorate salts) under similar experimental conditions (S7–S12, ESI[†]).

On successive addition of aqueous solution of Hg^{2+} (2.85×10^{-7} to 4.85×10^{-5} M) to solution of **1a** (3×10^{-5} M, in CH_3CN), the absorbance of **1a** at 227 and 291 nm gradually disappear accompanied by the progressive appearance of new bands at 260, 325 and 458 nm with two isosbestic points at 238 and 296 nm. These absorbance changes reached the saturation point at the addition of 4.28×10^{-5} M solution of Hg^{2+} ions. It is noteworthy that the addition of excess Hg^{2+} ions caused no significant changes in the UV-vis spectral pattern (Fig. 1(i)). The low energy band at 458 nm induces a color change (Fig. S10, ESI[†]) from colorless to bright yellow, well appreciated by the ‘naked eye’. The incremental addition of aqueous solution of Cu^{2+} ions to the solution of **1a** under similar experimental conditions resulted in the disappearance of the band at 291 nm accompanied by a progressive appearance of new bands at 288, 325, 433 and 517 nm which attained saturation at the addition of 4×10^{-5} M solution of Cu^{2+} ions (Fig. 1(ii)). The low energy bands are responsible for the color change (Fig. S10, ESI[†]) from colorless to red. The resulting titration data fit nicely with a 1 : 1 (**1a** : M^{2+}) binding model as suggested by HypSpec,¹⁹ a non-linear least-squares fitting programme, giving binding constant values, $\log \beta_{1:1} = 5.49$ and 5.23 for Hg^{2+} and Cu^{2+} , respectively. The 1 : 1 stoichiometry was further confirmed by Job’s plots (a continuous variation method) where the absorbance at 458 (Hg^{2+}) and 517 nm (Cu^{2+}) got to maximum when molar fraction of both the metal ions were 0.5 (Fig. 1, insets). The calculated detection limits²⁰ are 7.67×10^{-6} and 7.74×10^{-6} M for Hg^{2+} and Cu^{2+} respectively.

The fluorescence emission band of **1a** at 500 nm undergoes partial quenching on incremental addition of aqueous solution of

Hg^{2+} ions (1.42×10^{-6} to 3.85×10^{-5} M) (Fig. 2(i)) while complete quenching on successive addition of aqueous solution of Cu^{2+} ions (1.42×10^{-6} to 4×10^{-5} M) (Fig. 2(ii)).

The quenching of emission band is attributed to the spin orbit coupling effects in case of Hg^{2+} ions²¹ and the paramagnetic nature of Cu^{2+} .²² However, almost similar values of binding constants for Hg^{2+} ($\log \beta_{1:1} = 5.08$) and Cu^{2+} ($\log \beta_{1:1} = 5.20$) are indicative of equal magnitude of their interactions with **1a** which is further supported by the electrochemical studies. The

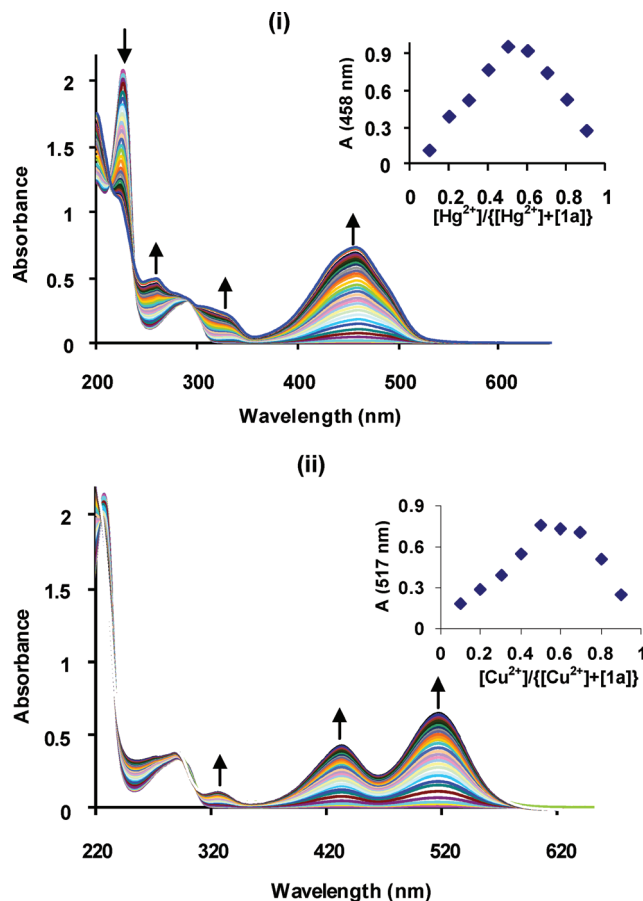


Fig. 1 Changes in the absorption spectrum of **1a** [3×10^{-5} M in CH_3CN] upon titration with aqueous solution of (i) Hg^{2+} (2.85×10^{-7} to 4.85×10^{-5} M) and (ii) Cu^{2+} (2.85×10^{-7} to 4.28×10^{-5} M). Inset: Job plots.

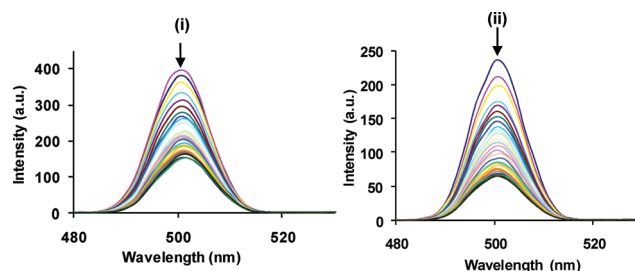


Fig. 2 Changes in the fluorescence spectrum of **1a** [3×10^{-5} M in CH_3CN] upon titration with aqueous solution of (i) Hg^{2+} (1.42×10^{-6} to 3.85×10^{-5} M), (ii) Cu^{2+} (1.42×10^{-6} to 4×10^{-5} M).

oxidation wave exhibited by **1a** at $E_{1/2} = 0.951$ V, attributed to the oxidation involving 2,3-double bond electron density,²³ shows an anodic shift almost of similar magnitude on the successive additions of solutions of Hg^{2+} and Cu^{2+} ions (S13 and S14, ESI†).

The successive addition of aqueous solution of Hg^{2+} (2.85×10^{-6} to 6.28×10^{-5} M) to solution of **1b** (3×10^{-5} M, in CH_3CN), causes the absorbance of **1b** at 228 and 291 nm to disappear gradually with concomitant appearance of new bands at 254, 315 and 467 nm with the isosbestic points at 240, 269 and 296 nm. These changes reached their maximum at the addition of 5.71×10^{-5} M solution of Hg^{2+} ions (Fig. 3(i)). On the other hand, the stepwise addition of aqueous solution of Cu^{2+} (2.85×10^{-7} to 4.28×10^{-5} M) induced the disappearance of 291 nm band with the concomitant appearance of new bands at 285, 325, 425 and 506 nm attaining saturation at the addition of 4×10^{-5} M solution of Cu^{2+} ions, with the isosbestic point at 303 nm (Fig. 3(ii)). Color change (Fig. S11, ESI†) from colorless to dark yellow (Hg^{2+}) and orange (Cu^{2+}) facilitate the 'naked eye' detection of these ions.

The calculated detection limits are 9.96×10^{-6} and 1.24×10^{-5} M for Hg^{2+} and Cu^{2+} respectively. The 1 : 1 stoichiometry

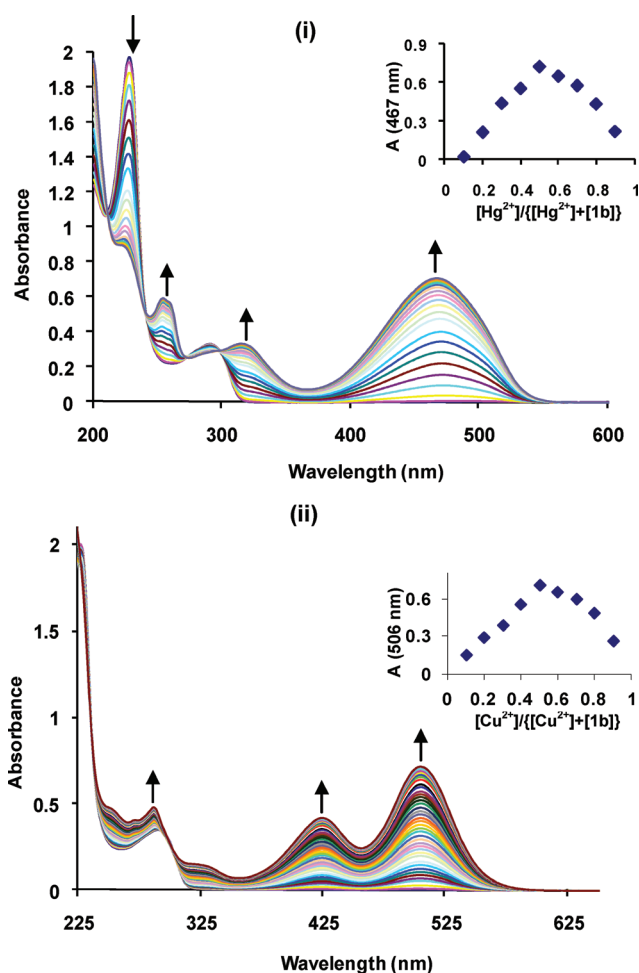


Fig. 3 Changes in the absorption spectrum of **1b** [3×10^{-5} M in CH_3CN] upon titration with aqueous solution of (i) Hg^{2+} (2.85×10^{-6} to 6.28×10^{-5} M) and (ii) Cu^{2+} (2.85×10^{-7} to 4.28×10^{-5} M). Inset: Job plots.

with the binding constant values $\log \beta_{1:1} = 6.27$ (Hg^{2+}) and 5.17 (Cu^{2+}) was established by Job's plots (Fig. 3, insets) and fitting the titration data by using HypSpec fitting programme. Like **1a**, **1b** exhibiting emission band at 500 nm, also displayed fluorescence quenching upon the addition of Hg^{2+} (2.85×10^{-6} to 6×10^{-5} M) and Cu^{2+} (2.85×10^{-6} to 3.71×10^{-5} M) under similar experimental conditions (S15 and S16, ESI†). The large difference in the $\log \beta_{1:1}$ values for Hg^{2+} (7.23) and Cu (5.01) suggest the stronger interaction of Hg^{2+} than Cu^{2+} with **1b**, attributed to the thiophilic nature of Hg^{2+} .²⁴ The proposed magnitude of interaction is further corroborated by a considerable perturbation in the oxidation wave at $E_{1/2} = 0.959$ V by Hg^{2+} as compared to Cu^{2+} (Fig. 4).

In contrast to **1a** and **1b**, which respond to the presence of both Hg^{2+} and Cu^{2+} , **1c** responds only to the presence of Cu^{2+} . The successive addition of aqueous solution of Cu^{2+} (2.85×10^{-6} to 4.28×10^{-5} M) to a solution of **1c** (3×10^{-5} M, in CH_3CN) induces a gradual disappearance of the original absorption bands at 227 and 292 nm accompanied by the appearance of new bands at 285, 378 and 508 nm with an isosbestic point at 308 nm attaining saturation at the addition of 4×10^{-5} M solution of Cu^{2+} ions (Fig. 5). These changes are accompanied by color change (Fig. S12, ESI†) from colorless to pink with the detection limit 6.7×10^{-6} M.

Obvious quenching of the emission band at 500 nm was observed on the incremental addition of aqueous solution of

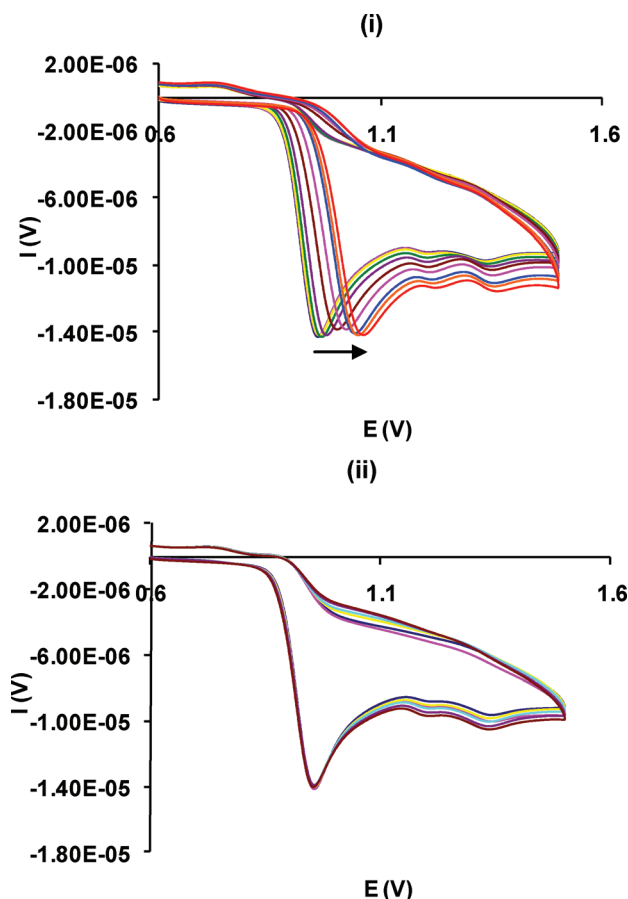


Fig. 4 Cyclic voltammograms changes of **1b** [5×10^{-4} M in CH_3CN] upon titration with aqueous solution of (i) Hg^{2+} (5×10^{-6} M to 4.5×10^{-5} M) and (ii) Cu^{2+} (5×10^{-6} M to 2.5×10^{-5} M).

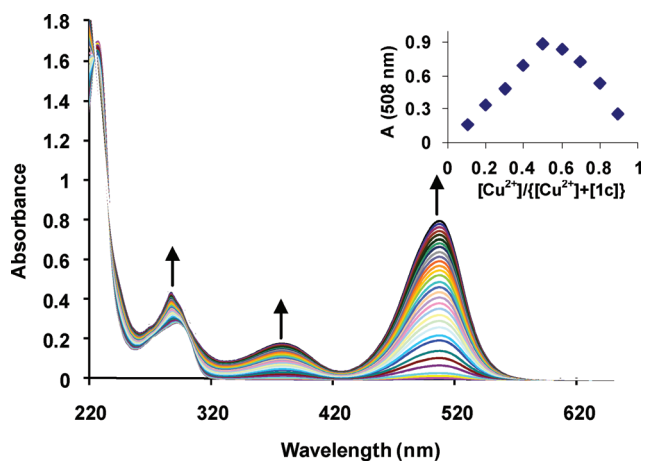


Fig. 5 Changes in the absorption spectrum of **1c** [3×10^{-5} M in CH_3CN] upon titration with aqueous solution of Cu^{2+} (2.85×10^{-7} to 4.28×10^{-5} M). Inset: Job plot.

Cu^{2+} ions (1.42×10^{-6} to 4.28×10^{-5} M) to a solution of **1c** (3×10^{-5} M in CH_3CN) (S17, ESI[†]). Fitting of both the titration data using HypSpec fitting programme, absorption as well as fluorescence, gave the binding constant values $\log \beta_{1,1}$ for 1 : 1 stoichiometry of 5.21 and 5.22, respectively. This stoichiometry was further confirmed from the Job's plot (Fig. 5, inset). No shift in the oxidation and reduction wave at $E_{1/2} = 0.927$ and $E_{1/2} = 0.846$ V was observed upon successive addition of Cu^{2+} ions (S18, ESI[†]).

^1H NMR experiments were performed to further study the responses of **1a–c** towards Hg^{2+} and Cu^{2+} ions. In the presence of Hg^{2+} and Cu^{2+} , while the aromatic protons of **1a–c** exhibit considerable shifts [from δ 6.01–7.47 to 6.79–9.14], the signals of C2–H [δ 6.66–6.86], were displaced to maximum to merge with the signals of aromatic protons indicating the interaction of enamine subunits involving N(Me)–C2H–C3 with the metal ions. The N–Me signals also depicted a downfield shift [from δ 3.63–3.70 to 4.0–4.23] corroborating the proposed interaction (see S19–S23, ESI[†]).

The development of molecules that can operate Boolean operations to form molecular gates has attained an increasing interest in the recent years. Out of 16 logic gates developed so far on the basis of Boolean operations (S24, ESI[†]), the main reports are on the commutative operations: AND/NAND (G_1/G_{14}), OR/NOR (G_7/G_8) and XOR/EQU (G_6/G_9) as well as the two of the non-commutative INHIBIT (G_2/G_4) gates. The other two noncommutative gates, *i.e.* IMPLICATION (G_{11}/G_{13}), with limited reports, are still unexplored. The IMPLICATION operations are important because they are equivalent to IF-THEN operation and the NOT operation and are obtained when $\text{In}_A = \text{In}_B = 0 \rightarrow \text{Out} = 1$ which is only quenched, *i.e.* $\text{Out} = 0$, in the presence of one input alone and further gets retrieved, *i.e.* $\text{Out} = 1$ when $\text{In}_A = \text{In}_B = 1$.

On the basis of our preliminary investigations we could generate IMPLICATION gate operating in fluorescence mode with only **1b** using Hg^{2+} and I^- as the two chemical inputs. As discussed above, the titration of **1b** with a solution of Hg^{2+} ions (5.71×10^{-5} M), the emission band at 500 nm gets quenched. Upon addition of aqueous solution of I^- ions (2.84×10^{-4} M) the original band at 500 nm gets recovered. Moreover, the

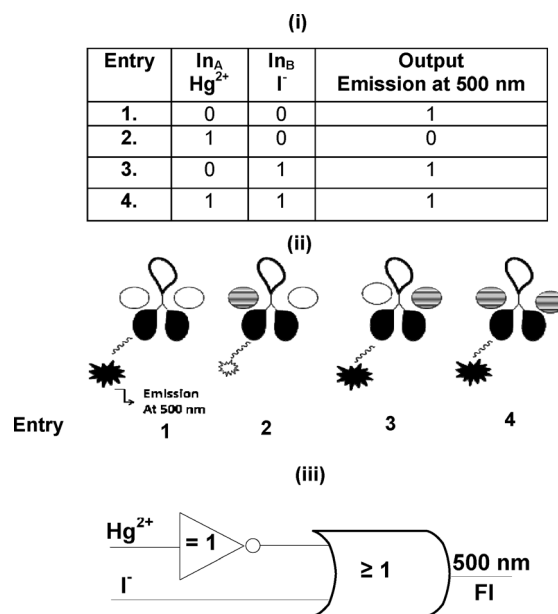


Fig. 6 Truth table and molecular circuit generated upon the addition of Hg^{2+} and I^- to **1b**.

addition of only I^- ion solution (5.71×10^{-5} M) to a solution of **1b** under similar experimental conditions caused no change in the emission band (Fig. 6). Consequently, previously rarely reported IMPLICATION logic function can be developed with respect to the emission band at 500 nm as output which can be represented as an OR gate with Hg^{2+} input (In_A) line containing an inverter. On the basis of above studies we suggest that possible mode of interaction of Hg^{2+} and Cu^{2+} with **1a–c** involves the π -system of bis(*N*-methylindolyl)methane unit²⁵ in addition to the interaction with oxygen and sulfur atoms of the furan and thiophene units of **1a** and **1b**, respectively. The mechanism by which IMPLICATION gate functions is suggested to be based on the formation of a stable mercury-iodide complex²⁶ that causes the displacement of Hg^{2+} from **1b**: Hg^{2+} complex formed in solution.

The results presented above demonstrate that the interaction of Hg^{2+} and Cu^{2+} with the bis(*N*-methylindolyl)methane-based derivatives leads to the color changes as a consequence of perturbations in their spectral behaviour. The interaction mechanism has been proposed to involve the π -electron system of bis(*N*-methylindolyl)methane unit as well as the heteroatoms present. Further, the changes in the fluorescence behaviour of one of the derivatives on employing Hg^{2+} and I^- ions as two chemical inputs has led to previously rarely reported IMPLICATION gate.

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