Bis(N-methylindolyl)methane based chemical probes for Hg$^{2+}$ and Cu$^{2+}$ and molecular IMPLICATION gate operating in fluorescence mode

Paramjit Kaur*\textsuperscript{a}, Sandeep Kaur\textsuperscript{a,b}, Kamaljit Singh*\textsuperscript{b}

\textsuperscript{a}Department of Chemistry, UGC-Center for Advance Studies-1, \textsuperscript{b}Organic Synthesis Laboratory, Deapartment of Applied Chemical Sciences and Technology, Guru Nanak Dev University, Amritsar-143005

Supporting Information
S1. Materials and Methods

1. Chemicals
All reagents were purchased from Sigma-Aldrich and aldehydes: furan-2-carbaldehyde, thiophene-2-carbaldehyde, benzaldehyde and N-methyl indole were used after fresh distillation. Dichloromethane (DCM) was dried over benzophenone ketyl under inert atmosphere and distilled directly in the reaction flask. Silica gel G (60-120 mesh) was used for column chromatography.

2. Instrumentation
UV-vis spectra were recorded on a SHIMADZU 1601 PC spectrophotometer, with a quartz cuvette (path length, 1 cm) and studies were performed in AR grade CH$_3$CN and double distilled water. The cell holder of the spectrophotometer was thermostatted at 25 $^\circ$C for consistency in the recordings. The fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer, with a quartz cuvette (path length, 1 cm). $^1$H and $^{13}$C NMR spectra were recorded on BRUKER Avance II 400 MHz spectrophotometer using CDCl$_3$, DMSO and CD$_3$CN as solvent and tetramethylsilane (SiMe$_4$) as internal standard. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, m = multiplet), integration, coupling constant J (Hz) and assignment. The mass spectra were recorded with Esquire 3000–00037 mass spectrometer. Elemental analyses were performed with a Thermo Flash EA 1112 analyser and were within ±0.4% of the theoretical values. IR spectra were recorded on Varian 660-IR Fourier-Transform IR Spectrophotometer in range 400-4000 cm$^{-1}$ using KBr as medium. Titration isotherms generated from UV-vis changes were fit in HypSpec fitting programme to establish the stoichiometry of the complex and to determine the binding constant. The pH titrations were performed with the Equip-Tronics Digital pH meter model-EQ 610. Electrochemical studies
were carried out on CHI 660C Electrochemical Workstation with a conventional three-electrode configuration consisting of platinum working (2 mm diameter) and counter electrodes and Ag/AgCl as reference electrode. The experiments were carried out in solution of sample in CH$_3$CN containing tetrabutylammonium perchlorate (TBAP) as supporting electrolyte at room temperature. Deoxygenation of the solutions was achieved by bubbling nitrogen for 10 min and the working electrode was cleaned after each run. The voltammograms were recorded with a scan rate of 100 mVs$^{-1}$.

**S2. Synthesis of 1a-c (Scheme 1)**

The compounds 1a-c were prepared by the condensation reactions of aldehydes: furan-2-carbaldehyde, thiophene-2-carbaldehyde, benzaldehyde (1 mmol) with N-methylindole (3 mmol), catalysed by amberlyst 15 (20 mg) (Scheme 1). After completion (TLC), the reaction mixture was allowed to cool at room temperature and diluted with dichloromethane, filtered and concentrated under vacuum. The residues were chromatographed on silica gel 60-120 mesh to isolate the corresponding products, the formations of which were confirmed from various spectroscopic data.

![Scheme 1. Synthesis of 1a-c.](image)

**3,3’-(furan-2-yl-methylene)bis-(1-methyl-1H-indole) (1a):** Yield: 96%; m.p. 121°C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.47 (2H, m, ArH), 7.35 (1H, m, ArH), 7.28-7.30 (2H, m, ArH), 7.18-7.22 (2H, m, ArH), 7.01-7.05 (2H, m, ArH), 6.74 (2H, s, ArH), 6.29-6.30 (1H, m, ArH), 6.05-6.06 (1H, m, ArH), 5.92 (1H, s, $meso$-CH), 3.70 (6H, s, CH$_3$); $^{13}$C NMR (100 MHz, DMSO): δ 152.6, 136.5, 136.4, 132.5, 122.9, 122.4, 116.7, 115.0, 114.0, 110.9, 105.3, 104.4, 101.7, 29.1, 28.0; $v_{max}$/cm$^{-1}$: 1608 (C-N), 1471 (C=C), 1219, 1125, 1055, 1011 (CH, in-plane), 737 (CH, out-plane); Anal. Calcd. (%) for C$_{23}$H$_{20}$N$_2$O: C, 81.15; H, 5.92; N, 8.23; Found: C, 81.01; H, 5.73; N, 8.73; $m/z$ 363 (M$^+$ + 23).
3,3’-(thiophene-2-yl-methylene)bis-(1-methyl-1H-indole) (1b): Yield: 97%; m.p. 178°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.44-7.46 (2H, m, ArH), 7.27-7.29 (2H, m, ArH), 7.17-7.23 (2H, m, ArH), 7.12-7.14 (1H, m, ArH), 6.99-7.03 (2H, m, ArH), 6.88-6.91 (2H, m, ArH), 6.70 (2H, s, ArH), 6.14 (1H, s, $meso$-CH), 3.68 (6H, s, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.2, 137.3, 127.8, 127.1, 126.4, 125.0, 123.5, 121.5, 119.8, 118.8, 118.2, 109.1, 35.1, 32.7; $\nu_{\text{max}}$/cm$^{-1}$: 1609 (C-N), 1470 (C=C), 1197, 1053, 1005 (CH, in-plane), 739 (CH, out-plane); Anal. Calcd. (%) for C$_{23}$H$_{20}$N$_2$S: C, 77.49; H, 5.65; N, 7.86; Found: C, 77.23; H, 5.82; N, 7.47; m/z 355.2 (M$^+$-1).

3,3’-(phenylmethylene)bis-(1-methyl-1H-indole) (1c): Yield: 95%; m.p. 183°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33-7.38 (4H, m, ArH), 7.24-7.29 (4H, m, ArH), 7.17-7.22 (3H, m, ArH), 6.96-7.00 (2H, m, ArH), 6.51 (2H, s, ArH), 5.87 (1H, s, $meso$-CH), 3.66 (6H, s, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.4, 137.4, 128.7, 128.3, 128.2, 127.4, 126.0, 121.4, 120.0, 118.6, 118.2, 109.1, 40.1, 32.7; $\nu_{\text{max}}$/cm$^{-1}$: 1605 (C-N), 1472 (C=C), 1230, 1122, 1054, 1016 (CH, in-plane), 743 (CH, out-plane); Anal. Calcd. (%) for C$_{25}$H$_{22}$N$_2$: C, 85.71; H, 6.28; N, 8.00; Found: C, 85.96; H, 6.46; N, 7.71; m/z 373 (M$^+$+ 23)

S3. Spectroscopic Analysis of 1a-c.
$^{13}$C NMR spectrum of 1a

EI Mass spectrum of 1a
IR spectrum of 1a

\(^1\)H NMR spectrum of 1b
13C NMR spectrum of 1b

EI Mass spectrum of 1b

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

This journal is © The Royal Society of Chemistry 2012
IR spectrum of 1b

$^1$H NMR spectrum of 1c
$^{13}$C NMR spectrum of 1c

EI Mass spectrum of 1c
**Fig. S4.** Changes in the UV-vis spectrum of pH titration of 1a \([3 \times 10^{-5} \text{ M, in CH}_3\text{CN}]\) with both HCl and NaHCO$_3$ (0.01 M). Inset: Changes in the UV-vis spectrum of pH titration of 1a at 227 nm.
Fig. S5. Changes in the UV-vis spectrum of pH titration of 1b [3 × 10^{-5} M, in CH_{3}CN] with both HCl and NaHCO_{3} (0.01 M). Inset: Changes in the UV-vis spectrum of pH titration of 1b at 228 nm.

Fig. S6. Changes in the UV-vis spectrum of pH titration of 1c [3 × 10^{-5} M, in CH_{3}CN] with both HCl and NaHCO_{3} (0.01 M). Inset: Changes in the UV-vis spectrum of pH titration of 1c at 227 nm.
Fig. S7. Changes in UV-vis spectrum of 1a [3 x 10^{-5} M, in CH_{3}CN] after the addition of aqueous solution of Hg^{2+}, Cu^{2+} and other metal ions (8 x 10^{-5} M) recorded immediately after mixing.

Fig. S8. Changes in UV-vis spectrum of 1b [3 x 10^{-5} M, in CH_{3}CN] after the addition of aqueous solution of Hg^{2+}, Cu^{2+} and other metal ions (8 x 10^{-5} M) recorded immediately after mixing.

Fig. S9. Changes in UV-vis spectrum of 1c [3 x 10^{-5} M, in CH_{3}CN] after the addition of aqueous solution of Cu^{2+} and other metal ions (8 x 10^{-5} M) recorded immediately after mixing.
**Fig. S10.** Observed color changes of solutions of **1a** [3 x 10^{-5} M, in CH$_3$CN] in the presence of aqueous solution of Hg$^{2+}$, Cu$^{2+}$ and other metal ions (8 x 10^{-5} M).

**Fig. S11.** Observed color changes of solutions of **1b** [3 x 10^{-5} M, in CH$_3$CN] in the presence of aqueous solution of Hg$^{2+}$, Cu$^{2+}$ and other metal ions (8 x 10^{-5} M).

**Fig. S12.** Observed color changes of solutions of **1c** [3 x 10^{-5} M, in CH$_3$CN] in the presence of aqueous solution of Hg$^{2+}$, Cu$^{3+}$ and other metal ions [8 x 10^{-5} M].
**Fig. S13.** Cyclic Voltammetric changes of 1a [5 x 10^{-4} M in CH_{3}CN] upon titration with aqueous solution of Hg^{2+} (2 x 10^{-6} M to 1.2 x 10^{-5} M).

**Fig. S14.** Cyclic Voltammetric changes of 1a [5 x 10^{-4} M in CH_{3}CN] upon titration with aqueous solution of Cu^{2+} (2 x 10^{-6} M to 1.2 x 10^{-5} M).
Fig. S15. Changes in the fluorescence spectrum of 1b [3 x 10^{-5} M in CH_{3}CN] upon titration with aqueous solution of Hg^{2+} (2.85 x 10^{-6} to 6 x 10^{-5} M).

Fig. S16. Changes in the fluorescence spectrum of 1b [3 x 10^{-5} M in CH_{3}CN] upon titration with aqueous solution of Cu^{2+} (2.85 x 10^{-6} to 3.71 x 10^{-5} M).
**Fig. S17.** Changes in the fluorescence spectrum of 1c \([3 \times 10^{-5} \text{ M in CH}_3\text{CN}]\) upon titration with aqueous solution of Cu\(^{2+}\) \((1.42 \times 10^{-6} \text{ to } 4.28 \times 10^{-5} \text{ M})\).

**Fig. S18.** Cyclic Voltammetric changes of 1c \([5 \times 10^{-4} \text{ M in CH}_3\text{CN}]\) upon titration with aqueous solution of Cu\(^{2+}\) \((5 \times 10^{-6} \text{ M to } 3.5 \times 10^{-5} \text{ M})\).
Fig. S19. $^1$H NMR spectrum of 1a (i) before and (ii) after addition of Hg$^{2+}$ ions.
Fig. S20. $^1$H NMR spectrum of 1a (i) before and (ii) after addition of Cu$^{2+}$ ions.
Fig. S21. $^1$H NMR spectrum of 1b (i) before and (ii) after addition of Hg$^{2+}$ ions.
Fig. S22. $^1$H NMR spectrum of 1b (i) before and (ii) after addition of Cu$^{2+}$ ions.
Fig. S23. $^1$H NMR spectrum of 1c (i) before and (ii) after addition of Cu$^{2+}$ ions.
### Table of Boolean operations for two inputs

<table>
<thead>
<tr>
<th>Gate No.</th>
<th>Operation No.</th>
<th>Commutative to operation no.</th>
<th>Result for A = 0 B = 0</th>
<th>Result for A = 0 B = 1</th>
<th>Result for A = 1 B = 0</th>
<th>Result for A = 1 B = 1</th>
<th>Logic gate</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>G₀</td>
<td>0</td>
<td>15</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Zero</td>
<td>‘0’ constant</td>
</tr>
<tr>
<td>G₁</td>
<td>1</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>AND</td>
<td>A and B</td>
</tr>
<tr>
<td>G₂</td>
<td>2</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>INHIBIT</td>
<td>A excluding B</td>
</tr>
<tr>
<td>G₃</td>
<td>3</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>ID A</td>
<td>A</td>
</tr>
<tr>
<td>G₄</td>
<td>4</td>
<td>-</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>INHIBIT</td>
<td>B excluding A</td>
</tr>
<tr>
<td>G₅</td>
<td>5</td>
<td>10</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>ID B</td>
<td>B</td>
</tr>
<tr>
<td>G₆</td>
<td>6</td>
<td>9</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>XOR</td>
<td>Either A or B</td>
</tr>
<tr>
<td>G₇</td>
<td>7</td>
<td>8</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>OR</td>
<td>A or B</td>
</tr>
<tr>
<td>G₈</td>
<td>8</td>
<td>7</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>NOR</td>
<td>Neither A nor B</td>
</tr>
<tr>
<td>G₉</td>
<td>9</td>
<td>6</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>EQU</td>
<td>A equivalent to B</td>
</tr>
<tr>
<td>G₁₀</td>
<td>10</td>
<td>5</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>INV B</td>
<td>Not B</td>
</tr>
<tr>
<td>G₁₁</td>
<td>11</td>
<td>-</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>IMPLICATION</td>
<td>B implies A</td>
</tr>
<tr>
<td>G₁₂</td>
<td>12</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>INV A</td>
<td>Not A</td>
</tr>
<tr>
<td>G₁₃</td>
<td>13</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>IMPLICATION</td>
<td>A implies B</td>
</tr>
<tr>
<td>G₁₄</td>
<td>14</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>NAND</td>
<td>Not both A and B</td>
</tr>
<tr>
<td>G₁₅</td>
<td>15</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>ONE</td>
<td>‘1’ constant</td>
</tr>
</tbody>
</table>