Mn(I)-based photoCORMs for trackable, visible light-induced CO release and photocytotoxicity to cancer cells

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1. Experimental Section and Measurements Procedure.

1.1. Physical Measurements

Molar conductivity measurements were done by using a EUTECH INSTRUMENT CON 510 (India) conductivity meter. UV-vis and emission spectra for the complexes were recorded in Perkin-Elmer UV/VIS spectrometer and HITACHI F-7000 Fluorescence spectrophotometer respectively. Solid-phase FT-IR spectra were recorded using Perkin-Elmer UATR TWO FT-IR Spectrometer operating from 400 to 4000 cm<sup>-1</sup>. NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer, using CDCl<sub>3</sub> and DMSO-d<sub>6</sub> as solvent and tetramethylsilane (TMS) as the internal standard. Q-TOF ESI Mass spectra (MS) were recorded in Bruker Esquire 3000 Plus spectrophotometer (Bruker-Franzen Analytic GmbH, Bremen, Germany). Time-correlated single-photon-counting (TCSPC) spectrometer (Horiba Jobin Yvon) was used to perform fluorescence lifetime measurement in which nanosecond laser of 375 nm was used as the excitation source in the following decay kinetics and data were analysed by a bi-exponential fitting program using IBH DAS-6 decay analysis software considering reduced chi-square value. The absorbance reading of MTT assays was collected using a Molecular Devises VersaMaxtunable microplate reader. All Theoretical calculations (DFT or TD-DFT) on all the ligand and complexes were carried out using Gaussian 09 rev. A.02. The input files to Gaussian 09 were prepared with Gauss view 5.0.8. Schematic drawing of the compounds and IUPAC names of all the ligands (L<sub>1</sub>-L<sub>4</sub>) were obtained by using ChemDrawProfessional 15.

1.2. Photolysis experiments
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IR, UV-visible and fluorescence spectroscopy studied Photo-induced release CO from the photoCORMs (1-4). The apparent rates ($k_{CO}$) of CO release from the complexes (1-4) dissolved in MeCN on exposure to the visible light (400-700 nm, 10 Jcm$^{-2}$) were measured by using 10mm path length quartz cuvette. The cuvette was placed at a distance of 1 cm from the light source. CO release was followed at a 350nm wavelength of respective complexes, and the log of the concentration of the complex was plotted against time. The absorbance versus time plots was fitted to the three parameters exponential equation $A(t) = A_\infty + (A_0 - A_\infty) \exp\{-k_{CO}t\}$, where $A_0$ and $A_\infty$ are the initial and final absorbance values, respectively. The apparent rate of CO loss ($k_{CO}$) was calculated from the ln(C) versus time (T) plot for each metal carbonyl complex. The apparent CO released also confirmed by myoglobin assay [1].

1.3. Luminescence Experiments

The luminescence spectra of the complexes (1-4) in acetonitrile at the concentration of 250µM were recorded in a quartz cuvette (1 cm x 1 cm) at room temperature. The complexes (1-4) were excited at 345 nm (1), 347 nm (2), 410 nm (3) and 350 (4) respectively to obtain luminescence spectra.

1.4. Myoglobin assay

Myoglobin from equine skeletal muscle was dissolved in phosphate buffered saline (PBS, 100 mM, pH 7.4) and reduced by adding sodium dithionite. The concentration of the deoxymyoglobin (Mb) generated was calculated from the absorbance of the Soret band at 434 nm. Next, 1-4 in MeOH were added to Mb, and the absorbance was taken after 5 min to ensure that the myoglobin was still reduced. On the basis of the Mb concentration, we added a MeOH solution of complex-4 (50Mm) to the Mb solution, and the initial absorbance was taken within 1 min then the absorbance was taken after 30 min. Finally, Carbonyl myoglobin (Mb-CO) produced. A shift in $\lambda_{max}$ from 434 to 422 nm was observed in each case because
of the formation of the Mb-CO. Final concentrations of Mb-CO were assessed at 424 nm and compared to the initial Mb present in the solution to quantify CO release by each compound.

1.5. DFT and TD-DFT Calculations

Theoretical calculations on all the ligands (L₁-L₄) and complexes (1-4) were carried out with density functional theory (DFT) and time-dependent density functional theory (TD-DFT) by using Gaussian 09 rev. A.02[2]. The input files were prepared with Gauss view 5.0.8. The structures of all the complexes (1-4) and ligands (L₁-L₄) in their ground state was optimized at the B3LYP/GEN level by using 6-31G(d,p) basis set for H, C, N, O, S atoms and LANL2DZ basic set for Mn atom in the gaseous phase. Using the DFT and TD-DFT calculation were performed to predict the electronic spectrum, and photo-induced CO release at the photo-activated states of the complexes. Gauss Sum was used to calculate the fractional contributions of various groups to each molecular orbital and also the contribution of percentage metal and ligands character involve corresponding in the HOMO and LUMO orbital [3].

After optimization of complex-4 (DFT), we performed TD-DFT calculation using B3LYP/GEN level by using 6-31G(d,p) basis set for H, C, N,O,S atoms and LANL2DZ basic set for Mn(I) to understand the excited state chemistry of the complex-4. At first we optimized singlet 1st, 2nd 3rd and 4th excited state of the complex-4, then we assign most populated electronic excited state (3rd excited state) based on experimental result. Further we optimized 1st, 2nd and 3rd excited triplet state using same basis function. From the optimized results we assign that electron jump from 3rd excited singlet state to 2nd excited triplet state via inter system crossing (ISC) because the lower energy difference between these two corresponding states. We observe significant increase in bond length for one of the Mn(I)-CO bond. Based on the literature survey we assumed that the solvent molecule (H₂O) occupied that vacant position of the complex 4 and Mn(I) converted to Mn(II) then again we optimized
the proposed 1\textsuperscript{st} and 2\textsuperscript{nd} triplet excited state using same basis function. Finally we observed simultaneous elongation for all the remaining Mn(II)-CO bond along with the Mn(II)-N and Mn(II)-O bonds in 2\textsuperscript{nd} triplet excited state. Such elongation in metal to ligand bond might led to disintegration of the complex 4 into Mn(II), ligands and CO. The final observation was supported by reference 39 in the manuscript.

1.6. Cell Culture, Cell Viability Assay and Flow Cytometry Analysis

The 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay was performed to determine the photocytotoxicity of the complexes (1-4) [4]. The MTT assay was based on the ability of mitochondrial dehydrogenases of viable cells in cleaving the tetrazolium rings of MTT with the formation dark purple, cell impermeable formazan crystals, soluble in DMSO which could be quantified from by UV-visible spectroscopy. Approximately, 5000 cells of human cervical carcinoma (HeLa) cells, were plated separately in two different 96 wells culture plate and incubated with the complexes and the ligands dissolved in 1% DMSO/Dulbecco’s 6 modified Eagle’s medium (DMEM) in a dose-dependent manner (0.78 to 50 μM) for 4 h in the dark. After 4 h of initial incubation in the dark, the media was removed and replaced with DPBS buffer. One set of the cells were exposed to visible light (0, 5, 15 and 30 min exposure, \( \lambda = 400-700 \text{ nm} \), light dose = 10 J cm\(^{-2} \) ) using a Luzchem Photoreactor (Model LZC-1, Ontario, Canada) fitted with 8 fluorescent white tubes of Sylvania make in one of the plates, whereas the other set was kept in the dark for 0.3 hunder similar experimental condition. After photo-exposure, the DPBS was removed and replaced with fresh medium and incubation was continued for a further period of 19 h followed by the addition of 5 mg/mL of MTT (25 μL) to each well and incubated for an additional 3 h. The media was removed entirely from the wells, and DMSO (200 μL) was
added. Absorbance was recorded at 570 nm using TECAN microplate reader. Cytotoxicities of the complexes (1-4) was measured as the percentage ratio of the absorbance of the treated cells to the untreated controls. The IC\textsubscript{50} values were determined by nonlinear regression analysis (Graph Pad Prism 6). Data were obtained by using three independent sets of experiments done in triplicate for each concentration. Using the luminescent property of complex 4, the CO release study was further done by using flow cytometric study. Human cervical carcinoma cells were seeded appropriately (3.0 × 10\textsuperscript{5}) in 6 well plates and cultured for 24 h. Complex 4(30\textmu M) was pre-incubated with HeLa cells in the dark for 4 h then washed twice with PBS buffer and finally time-dependent photoirradiation (0, 5, 15 and 30 min exposure, λ = 400-700 nm, light dose = 10 J cm\textsuperscript{-2}) were done keeping one identical set in the dark in the same condition. The assay was performed after 19 h of incubation, the cells were trypsinization, and a single cell suspension was prepared. The fluorescence (green fluorescence of Annexin V-FITC dye) of the cells was measured with a flow cytometer (FACS canto, Beckton Dickenson)[5].

References


Supporting Information


Table S1. Selected Mn(I) to ligand bond length of the complex 4 at different excited states determined from DFT and TD-DFT calculations at TDDFT/B3LYP/6-31G(d,p)/LanL2DZ level.

<table>
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<tr>
<th>Complex-4 States</th>
<th>Bond Length</th>
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<tr>
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<td>Mn-N</td>
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<tr>
<td>Ground State (S(_0))</td>
<td>1.8912</td>
</tr>
<tr>
<td>Excited State (S(_1))</td>
<td>1.8912</td>
</tr>
<tr>
<td>Triplet State (T(_1))</td>
<td>1.8909</td>
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<tr>
<td>Triplet State (T(_2))</td>
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<tr>
<td>Triplet State (T(_2^*))(^a)</td>
<td>1.9450</td>
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</tbody>
</table>

\(^a\)Refer to Figure 4. The bond lengths of concerned for photo-activated release of CO were made bold.

Table S2. MTT data of all complexes in visible light exposure (400-700 nm, 10 J cm\(^{-2}\)).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Dark IC(_{50}) [(\mu m)]</th>
<th>5 min. Light IC(_{50}) [(\mu m)]</th>
<th>15 min. Light IC(_{50}) [(\mu m)]</th>
<th>30 min Light IC(_{50}) [(\mu m)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>57.13</td>
<td>48.12</td>
<td>41.81</td>
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<td>4</td>
<td>56.25</td>
<td>26.81</td>
<td>7.696</td>
<td>7.295</td>
</tr>
</tbody>
</table>
Figure S1. $^1$H NMR of L$^1$ recorded in DMSO-d$_6$ using Bruker Avance 400 (400 MHz) spectrometer.

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Figure S14. Q-TOF ESI Mass spectra of the L\textsuperscript{2} recorded in CH\textsubscript{3}CN using Bruker Esquire 3000 Plus spectro-photometer (Bruker-Franzen Analytic GmbH, Bremen, Germany). The peak at m/z 340.1746 corresponds to the species [L\textsuperscript{2}H]\textsuperscript{+}.
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Figure S23. Q-TOF ESI Mass spectra of 3 recorded in CH₃CN using Bruker Esquire 3000 Plus spectro-photometer (Bruker-Franzen Analytic GmbH, Bremen, Germany). The peak at m/z 477.9653 corresponds to the species \([\text{Mn(L}^3\text{)(CO)}_3]\text{H}^+\) and m/z 499.1252 corresponds to the species \([\text{Mn(L}^3\text{)(CO)}_3]\text{Na}^+.\) The inset represents the corresponding isotopic distribution (experimental and calculated).

Figure S24. Q-TOF ESI Mass spectra of 4 recorded in CH₃CN using Bruker Esquire 3000 Plus spectro-photometer (Bruker-Franzen Analytic GmbH, Bremen, Germany). The peak at m/z 477.9653 corresponds to the species \([\text{Mn(L}^3\text{)(CO)}_3]\text{H}^+\). The inset represents the corresponding isotopic distribution (experimental and calculated).
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