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Synthesis of DPA based NNN donor ligands having piperidinyl groups and their platinum complexes towards potent anti-cancer applications

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Dipicolylamine (dpa) moiety has received much attention due to its coordination versatility. Our objective is to incorporate piperidinyl groups into the dpa system due to possibility of the piperidinyl group to target sigma receptors as it shows high affinity to sigma receptors, which are expressed in high densities in breast cancer cells. In this study, two novel ligands; N($(CH_2)_2$piperidine)dpa (L1) and N($(CH_2)_3$piperidine)dpa (L2) (Figure 1) were synthesized by utilizing pendant piperidinyl groups having different chain lengths. The platinum complexes of novel ligands; [PtClN($(CH_2)_2$piperidine) dpa]Cl (C1) and [PtClN($(CH_2)_3$piperidine)dpa]Cl (C2) were also synthesized during the study. Structural data obtained from single crystal X ray diffraction for C1 confirms that L1 serves as a tridentate donor ligand. UV visible spectra of both ligands and complexes were recorded in methanol. Absorption peaks in 200-300 nm range in UV visible spectra of ligands are due to intra ligand $\pi \rightarrow \pi^*$ transitions and peaks above 300 nm range are due to $n \rightarrow \pi^*$ transitions in the ligands. As expected, no absorption peaks corresponding to $n \rightarrow \pi^*$ transitions were observed in UV visible spectra of complexes due to lack of lone pairs in the coordination complexes. Methylene protons observed as a singlet (3.87 ppm) in ^{1}H NMR spectrum of L1. The N-H bond of secondary amine group present in dpa gives an IR band in 3310-3350 cm^{-1} region. However, IR spectra of both ligands and complexes gave no transmittance peaks in region 3310-3350 cm^{-1} confirming the absence of the N-H group which also confirms the formation of ligands and complexes. Both ligands displayed intense fluorescence in methanol. However, fluorescence spectra of platinum complexes showed lower intensities than the respective ligands, possibly indicating static quenching of fluorescence upon coordination to metal. These ligands and complexes can be explored towards treatment of breast cancer due to incorporation of piperidinyl group.

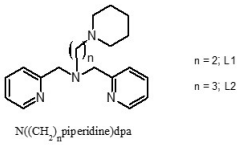

Figure 1: Line diagram of proposed ligands where n=2 for L1 and n=3 for L2

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