Morphological and in vitro evaluation of programmed cell death in MCF-7 cells by new organoruthenium(II) complexes

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Supporting Information

The IR spectra of the [HL\textsuperscript{1}-HL\textsuperscript{4}] ligands and its complexes provide information about the metal ligand bonding. A strong absorption at 1556-1637 cm\textsuperscript{-1} in the ligands [HL\textsuperscript{1}-HL\textsuperscript{4}] is assigned to the presence of \(\nu(C=N)\) group. This band undergoes a negative shift of 38-42 cm\textsuperscript{-1} in all the complexes, which can be attributed to the donation of alone pair of the nitrogen to the metal ion during the coordination.\textsuperscript{1,2} The ligand may exist in thione-thiol tautomerization since it contains a thioamide (-NH-C=S) functional group. The absence of the \(\nu(S-H)\) stretching frequency in the region 2500-2600 cm\textsuperscript{-1} and the presence of \(\nu(N-H)\) stretching frequency in the region 3231-3434 cm\textsuperscript{-1} in the IR spectrum of the ligand indicate thione form in the solid state. This is further inferred from the presence of a strong band in the region 826-863 cm\textsuperscript{-1} due to the \(\nu(C=S)\) stretching frequency which completely disappeared in the complex 4 and a new band appeared at 740 cm\textsuperscript{-1} corresponding to \(\nu(C=S)\) indicating the enolisation of NH-C=S group and subsequent coordination through the sulphur atom.\textsuperscript{3,4} However in complexes 1-3, the absence of the \(\nu(S-H)\) stretching frequency and presence of \(\nu(N-H)\) stretching frequency at 3011-3057 cm\textsuperscript{-1} indicate the involvement of the thione sulphur in the coordination rather than thiolate.\textsuperscript{5,6} The electronic spectra (Fig. S1) of the complexes have been recorded in CH\textsubscript{2}Cl\textsubscript{2} and they displayed two to three bands in the region around 242–349 nm. The bands appeared in the region 242–295 nm have been assigned to intra ligand transition,\textsuperscript{7} the bands around 309–349 nm were due to LMCT (s→d).\textsuperscript{8}
Fig. S1. Electronic absorption spectrum of complexes (1-4)

Fig. S2. $^1$H NMR spectrum of [H-Ac-tsc] (HL$^1$)
Fig. S3. $^{1}$H NMR spectrum of [RuCp(Ac-tsc)(PPh$_3$)].Cl (1)

Fig. S4. $^{13}$C NMR spectrum of [RuCp(Ac-tsc)(PPh$_3$)].Cl (1)
Fig. S5. $^1$H NMR spectrum of [H-Ac-mtsc] (HL$_2$)

Fig. S6. $^1$H NMR spectrum of [RuCp(Ac-mtsc)(PPh$_3$)].Cl (2)
Fig. S7. $^{13}$C NMR spectrum of [RuCp(Ac-mtsc)(PPh$_3$)].Cl (2)

Fig. S8. $^1$H NMR spectrum of [H-Ac-etse] (HL$_3$)
Fig. S9. $^1$H NMR spectrum of [RuCp(Ac-etsc)(PPh$_3$)].Cl (3)

Fig. S10. $^{13}$C NMR spectrum of [RuCp(Ac-etsc)(PPh$_3$)].Cl (3)
Fig. S11. $^1$H NMR spectrum of [H-Ac-ptsc] (HL₄)

Fig. S12. $^1$H NMR spectrum of [RuCp(Ac-ptsc)(PPh₃)] (4)
Fig. S13. $^{13}$C NMR spectrum of [RuCp(Ac-ptsc)(PPh$_3$)] (4)

Fig. S14. Hydrogen bonding of [RuCp(Ac-mtsc)(PPh$_3$)].Cl (2)
Fig. S15. Molecular packing diagram of $[\text{RuCp}(\text{Ac-mtsc})(\text{PPh}_3)]\cdot\text{Cl}$ (2)

Fig. S16. Molecular packing diagram of $[\text{RuCp}(\text{Ac-ptsc})(\text{PPh}_3)]$ (4)
**Fig. S17.** Absorption titration spectra of fixed concentration (10 μM) of ligands (HL₁- HL₄) complexes 1-4 with increasing concentrations (0 - 50 μM) of CT-DNA (trisHCl buffer, pH 7.2).
**Fig. S18.** The emission spectra of the DNA–EB system ($\lambda_{\text{exc}} = 515 \text{ nm}, \lambda_{\text{em}} = 550–750 \text{ nm}$), in the presence of ligands (HL$^{1-4}$). [DNA] = 10 $\mu$M, [ligands] = 0-50 $\mu$M, [EB] = 10$\mu$M. The arrow shows the emission intensity changes upon increasing ligands concentration.

![Emission spectra of DNA–EB system](image1)

**Fig. S19.** The emission spectrum of BSA (10 $\mu$M; $\lambda_{\text{exc}} = 278 \text{ nm}; \lambda_{\text{em}} = 347 \text{ nm}$) in the presence of increasing concentration of ligands (0 – 50 $\mu$M). The arrow shows the emission intensity changes upon increasing ligands concentration.

![Emission spectrum of BSA](image2)
**Fig. S20.** Absorption titration spectra of ligands and complexes with BSA

**Fig. S21.** Synchronous spectra of BSA (10 μM) in the presence of increasing concentration of ligands $\text{HL}^1$-$\text{HL}^4$ for a wavelength difference of $\Delta\lambda = 60$ nm. The arrow shows the emission intensity changes upon increasing concentration of ligands.
Fig. S22. The emission spectrum of HSA (10 μM; λexc = 280 nm; λemi = 340 nm) in the presence of increasing concentration of ligands (0 – 50 μM). The arrow shows the emission intensity changes upon increasing ligands concentration.

Fig. S23. Absorption titration spectra of complexes with HSA
Emi\textit{sions in the env\textit{ironment (h\textit{gh)})}

- (HL\textsubscript{1})
- (HL\textsubscript{2})
- (HL\textsubscript{3})
- (HL\textsubscript{4})

(Emission intensity)

Wavelength (nm)
**Fig. S24.** Synchronous spectra of HSA (10 μM) in the presence of increasing concentration of Ligands (HL₁-HL₄) and complexes (1-4) for a wavelength difference of Δλ = 60 nm. The arrow shows the emission intensity changes upon increasing concentration of ligands.
**Fig. S25.** Stability of the complexes (1-4) in 0.2 % DMSO

**Table S1.** Comparative results of DNA, BSA, HSA binding and cytotoxicity studies

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<th>DNA Binding study</th>
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<th>HSA Binding study</th>
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References


